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Residues of antimicrobial agents and related compounds of emerging concern in manure, water and soil

Part 2 – Final data set of a pilot campaign and outline for an EU-wide monitoring assessment

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Foreword

The Laboratory of the Water and Marine Resources Unit investigates the occurrence and fate of chemical pollutants entering and travelling with the natural and urban water cycles. In doing so, the laboratory also characterises the possible treatment and removal options for such compounds. In particular the so-called Compounds of Emerging Concern (CECs) as well as their degradation and metabolisation products are of interest in its investigation.

The issue of veterinary medicinal products and in particular those of an antimicrobial effect have attracted interest while trying to understand the development and propagation of antimicrobial resistances.

Likewise, the recovery of resources and energy from waste related to animal husbandry, e.g. manures, slurries and alike is evolving into an important practice under the EU's Strategy for a Circular Economy. To steer a sustainable development into the right direction, it is important not only to understand the opportunities that arrive from a circular economy approach but also to manage the related circularity of risks related to it.

In order to improve the knowledge base the laboratory carries out an EU-wide assessment on processed manures as well as on waters exposed directly or indirectly to manure and derived fertilising products. Particular attention is given to the investigation of agricultural runoff, but also to the question to which extend such chemicals will enter either the food chain or other supply chains in case of reuse of the manure.

The findings are published in a series of technical reports in which this one is the second stepping-stone in building an enhanced knowledge base for the making and implementation of improved EU policies.

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Abstract

In a thinking of circular economy, the understanding of how problematic chemical substances may migrate and travel across the various boundaries of a life-cycle, is of pivotal importance to ensure that the philosophy of reuse and recycle is not jeopardized by new risks of contamination. Recycled nutrients from animal manure and slurry can replace nutrients from primary raw materials. The main challenge is to obtain recycled nutrient resources that have an equal or better environmental performance than the primary nutrient resources they replace. In this framework, veterinary medicinal products (VMP) and in particular the anti-microbial agents (AMAs) are a growing source of concern in the context of the reuse of processed manure as a fertilizer.

In order to prepare a larger and EU-wide monitoring exercise aiming at the characterisation of processed manure as well as on the waters exposed directly or indirectly to the (processed) manure, a first pilot exercise was organised to develop an appropriate protocol. While the first related report compiled a series of background information collected, the results on the analytical characterization of pilot sites operated by the Slovak University of Agriculture in Nitra are presented and discussed here.

Manure samples (processed and untreated), runoff, groundwater and surface water samples, were analysed for 488 compounds covering typical representatives of herbicides, fungicides, insecticides, pharmaceuticals, ingredients of personal care products and other industrially used chemicals. For 60 of these compounds (corresponding to 12 %), concentration above the established limits of quantification of these novel multi-compound technique were obtained.

The study demonstrates the applicability of the hybrid target / non-target analytical approach called "*Compound Fishing*" and the reports presents the design for a related EU-wide exercise. Although this study does not characterize the respective test sites, it delivers an understanding of environmental pressures created on sites and under real-field scenarios. The experimental work conducted allows also to establish a link between the evaluation of scientific literature, the biogeochemical modelling and the field conditions scenarios of when processed manure is applied.

1. Introduction

There is growing evidence that both, human and veterinary medicines are harmful to wildlife and ecosystem (Sebestyén *et al*., 2018). Thus anti-parasites can be excreted and affect adversely organisms living in or feed on dung (Liebig *et al.*, 2010). Charuaud *et al.* (2019) reviewed studies from 2007 to 2017 and identified sixty-eight veterinary pharmaceutical residues in natural waters reaching up concentrations as high as several micrograms per litre. While a great deal of information could be found on antibiotics, the authors reported a data gap on occurrence and fate of anti-parasitic drugs with special focus on tap waters.

Sandoz *et al.* (2018) provide an up-to-date review on most of the traditional dissemination pathways of pharmaceuticals used for veterinary purposes, including prophylaxis and growth promotion with focus on beef cattle farmyards. While transport of these compounds are generally investigated in relationship to manure management and soil application as well as the processes involved, the authors suggest that aerial transport and deposition may play a significant role, too, in particular in arid and semi-regions.

Consequently, Christou *et al.* (2018) suggest considering and studying these group of pharmaceuticals as an emerging risk with regard to phytotoxicity (largely unknown) and for agricultural sustainability, mainly due to the uncertainties related to combined effects in the chemical mixtures. Indeed, the review from Bottoni and Caroli (2018) on some 1000 papers, reports and other publicly available documents covering a three-year period (2014-2016) raises serious concern about the impact of pharmaceutical residues amongst others on food commodities. Among the different groups of compounds of emerging concern related to animal husbandry, it is obvious that veterinary antibiotics are of primary concern. Used in large scale and quantities, these substances are usually poorly sorbed in the animal gut and hence largely excreted unchanged or poorly metabolised in faeces and urine, making them an agro-ecological issue of planetary relevance (Kuppusamy *et al.*, 2018 and literature cited). The same review identifies the use of animal manure/urine either directly or after processing as primary cause for the release of veterinary antibiotics into the agro-ecosystem. Grenni and co-worker (2018) present well the current state of knowledge regarding the ecological effect of antibiotics on natural ecosystems with special focus on natural microbial communities in soil and water. Riaz *et al.* (2018) concentrated in their critical review on fluoroquinolones.

There is abundant evidence of the complex, yet clear relationship between the occurrence of antimicrobial resistances (AMR) and the use of antimicrobial agents. Scenarios forecast for a not too far future are indeed alarming. Thus, in 2016, de Kraker *et al.* (2016) estimated for the year 2050 a 10 000 000 annual deaths due to antimicrobial resistances. The same authors yet acknowledge the unreliability of such global estimates of the burden of AMR and called for detailed and reliable data "*preferably based on comprehensive, population-based surveillance data from low-, middle-, and high-income countries.*" In his commentary published in *The Lancet*, Asaduzzaman (2018) repeats his call for action and the need of a globally coordinated approach to tackle the antimicrobial resistance challenge, involving also an environmental mitigation strategy.

25 000 patients die annually in the EU alone as a result of infections caused by resistant bacteria and globally this number could be as high as 700 000 (EC, http://ec.europa.eu/health/amr/sites/amr/files/amr_factsheet_en.pdf). According to the same source, the bulk of antimicrobials are not consumed by humans, but by animals. In the US, the livestock sector accounts for about 80 % of total annual consumption. Between 2010 and 2030, global consumption of antimicrobials in the livestock sector is projected to increase by about 67 %.

According to an EMA ESVAC Report (2016), of the overall sales of antimicrobials in the 29 countries in 2014, the largest amounts, expressed as a proportion of mg/PCU, were accounted for tetracyclines (33.4 %), penicillins (25.5 %) and sulfonamides (11.0 %).

From the antimicrobial classes listed in the third World Health Organization (WHO) list of critically important antimicrobials (CIAs) with the highest priority in human medicine, the sales for food-producing animals of 3rd- and 4th-generation cephalosporins, fluoroquinolones and macrolides accounted for 0.2 %, 1.9 % and 7.5 %, respectively, of the total sales in the 29 countries participating in ESVAC in 2014. Overall, the sales of polymyxins (mg/PCU) accounted for 6.6 % of the total sales, with colistin representing more than 99 % of the sales of polymyxins. In other words, animal husbandry is an important source for antimicrobial substances reaching the environment.

As mentioned above, animal manure and urine play a crucial role in the release of veterinary medicinal agents and in particular antibiotics to the agro-environment. Due to the aforementioned poor sorption in the animal gut, active ingredients may be excreted even up to 90 percent, but may feature also much better uptake leading to release rates of below 5 % (Spielmeyer, 2018). The subsequent use of manure prior to application, e.g. as substrate in biogas plants, as well as enhanced re-valorisation techniques obviously alter the concentration of these substances.

Likewise, their presence may however also affect the productivity of the plant, e.g. by decreasing the microbial activity in a digester (Spielmeyer, 2018; Zhang *et al.*, 2019; Ezzariai *et al.,* 2018; Berendsen *et al.*, 2018; Bousek *et al.*, 2018). Bousek *et al.* (2018) postulate consequently a combination of different treatment processes for high antibiotic reduction and reported that unaccustomed anaerobic digestion is inhibited at low antibiotic concentrations. Fu *et al.* (2018) quantified the inhibition of an anaerobic manure digestion process through the presence of tetracycline. According to their findings, tetracycline presence leads to an 8.8 % of yield reduction for methane in the investigated AD reactor, an effect however, which was reduced to 4.8 % by the addition of calcium peroxide. The optimisation of degradation processes occurring to the anaerobic digestion step, was subject on another study aiming at amoxicillin (Liu *et al.,* 2018). Their results suggested a rather rapid degradation to this compound and its breakdown products.

The release of ammonia and the production of volatile fatty acids (VFA) are important in the process optimisation of high-solid anaerobic digestion. According to Sui *et al.* (2018 and literature cited), indeed, there is not only a relationship between the effect of exogenous inhibitors such as ammonia and VFA and the efficiency of the anaerobic digestion, but also on the occurrence of antibiotic resistance in digested pig manure.

In this setting, Spielmeyer (2018) draw the attention to the fact that although apparently high removal rates may be achievable through processing, degradation cannot be assumed automatically, since in many cases only minor structural modification of the parent substance led to still microbiologically active molecules.

Berendsen *et al.* (2018) investigated 46 different antibiotics in fortified manure samples after 24 days of incubation of manure from calves, pigs and broilers observing cases of persistence of up to a year in some cases.

Mullen *et al.* (2019) investigated plant uptake by Zea mays L. grown on manure-fertilized soil. Although tetracyclines tended to predominate in soil, a significantly larger plant bioaccumulation was observed for sulphonamides. However, the authors also confirmed that in none of the plant samples antimicrobial resistance genes were observed.

Albero and co-workers (2018) examined more in detail the relationship between persistence and availability of selected veterinary antibiotics in soil and soil-(poultry)manure systems concluding that the route of entry into the soil system, e.g. use of recycled water vs. manure application may play an important role as regards the soil availability of the such compounds. Thus, among the studied compounds sulfamethoxazole, sulfamethazine and lincomycin featured the highest soil availability, while levels of chlortetracycline, doxycycline, ciproflaxin and enrofloxacin in the soil aqueous was very low.

In a plant toxicity study, Sidhu *et al.* (2019a) assessed ciprofloxacin and azithromycin with regard to their transfer from biosolid-amended soil to three plants (radish – *Raphanus sativus*, lettuce – *Lactuca sativa*, tall fescue grass – *Festuca arundinacea*). According to their conclusions only minimal risks to plants and possible impact on human and/or the animal food chain exist. In a related study (Sidhu *et al.*, 2019b) ascribed this limited bioavailability to stronger adsorption to the organic matter of the biosolid.

The comparative analysis of 40 samples of cattle, pig and poultry manure, 65 related soil samples and 27 vegetation samples in an agricultural area in North-western Spain, however, detected significant number of antibiotic residues in 71 % of grass and corn samples (Conde-Cid *et al.*, 2018). In the same study, pig slurries featured the highest number and concentrations of antibiotics. The study of plant uptake of a wide range of compounds of emerging concern has been recently also reviewed by Pullagurala *et al.* (2018) and Madikizela *et al.* (2018), both high-lightening the role of veterinary medicinal agents.

Kivits and co-workers (2018) provided also evidence that veterinary antibiotics are indeed present in groundwater below agricultural areas in the Netherlands and linked this to the practice of spreading manure.

One of the approaches to reduce possible side effects in manure processing and to enhance nutrient and resource recovery is the combination of the anaerobic digestion step with the use of algae in a bio-refinery process (Chowdhury *et al.*, 2018). Manure-based algae-cultivation hence appears as a cost-effective tool in the management of digested manure (Deng *et al.*, 2018; Stiles *et al.*, 2018, Renuka *et al.*, 2018). Markou *et al.* (2018), however, critically discussed the need to address related contamination risks and biomass safety concern related in particular to the presence of xenobiotics in the manure used for these purposes.

While the first related report compiled a series of background information collected, the results on the analytical characterization of pilot sites operated by the Slovak University of Agriculture in Nitra are presented and discussed in the following sections. The pilot exercise aimed at the organisation of larger EU-wide assessment of processed manure, outline of which is also presented at the end.

Manure samples (processed and untreated), runoff, groundwater and surface water samples, were analysed for 488 compounds covering typical representatives of herbicides, fungicides, insecticides, pharmaceuticals, ingredients of personal care products and other industrially used chemicals. For 60 of these compounds (corresponding to 12 %), concentration above the established limits of quantification of these novel multi-compound technique were obtained.

Although this study does not allow characterizing the respective test sites, it delivers an understanding of environmental pressures created on sites and under real-field scenarios. The experimental work conducted permits to establish a link between the evaluation of scientific literature, the biogeochemical modelling and the field conditions scenarios of when processed manure is applied.

2. Multi-compound analytical methodology

All samples collected in this study were analysed for compounds listed in Table 1 of the Annex, including some five hundred chemicals belonging to different categories (i.e.: industry, personal care, pesticides and pharmaceuticals, etc.).

This selection includes also the compounds considered in the JRC technical Report "*Residues of antimicrobial agents and related compounds of emerging concern in manure, water and soil*", Part I Pilot-sampling campaign in Slovakia and first findings (Tavazzi *et al*., 2018).

The following environmental matrices, collected as described in Section 2.1 of Tavazzi *et al*., 2018, were processed with ad-hoc developed analytical procedures:

- cattle urine,
- non-processed manure,
- processed manure,
- soil,
- water samples including groundwater, run-off water and surface water.

2.1.1. Cattle urine for polar compounds extraction

A more specific procedure for urine sample extraction compared to protein precipitation was developed, which implies the use of SPE cartridge. The rationale was identified in the possible more accurate interferences' elimination provided by SPE with the aim of improving the selectivity of the entire procedure.

Cattle urine sample was allowed to equilibrate at room temperature, then vigorously hand-shaken. A 10 ml aliquot was diluted with 90 ml MilliQ water into a 100 ml glass bottle. 0.05 ml of internal standard mixtures at 1 µg/ml was added and the sample was vortex-mixed for 30 seconds.

The diluted sample was then extracted by SPE, using Oasis HBL cartridge (Waters, Milford, MA, USA), according to the procedure reported in Table 2, Annex I.

A sequential elution was performed with 6 ml ethyl acetate (1st fraction) followed by 6 ml methanol (2nd fraction). All used solvents were "*pesticide analysis*" grade.

The two fractions were mixed and evaporated to dryness. The sample was reconstituted in 0.5 ml reconstituting solution and analysed by UHPLC-MS/MS.

2.1.2. Cattle urine for apolar compounds extraction

Apolar compounds were extracted from cattle urine by Liquid–Liquid Extraction (LLE), using ethyl acetate as extraction solvent. The procedure was applied to a 20 ml cattle urine aliquot, opportunely diluted with 20 ml MilliQ water.

A 250 ml Erlenmeyer flask was used for LLE. Diluted sample was spiked with 0.2 ml of internal standards mixture at 1 µg/ml and then extracted with 50 ml of ethyl acetate, using a horizontal shaker (speed 110) for 20 minutes. After shaking, the sample was left to separate into two phases for 30 minutes. The extraction was repeated three times.

The ethyl acetate layer (top layer) was dried onto a 10 g anhydrous Na_2SO_4 column, previously prepared. After drying, 0.1 ml of syringe standard solution at 1 µg/ml was added and the sample evaporated to about 0.5 ml volume. The sample was then transferred into a 1.5 ml brown MS vial, using toluene and evaporated to a final volume of 0.2 ml, under gentle stream of nitrogen.

2.1.3. Non-processed manure for polar compounds extraction

Non-processed manure sample (humid weight 500 g) was freeze-dried using Heto DRYWINNER equipment, at -60 °C for two days at about 0.1 mmHg pressure.

Solid-Liquid Extraction (SLE) was performed on 1 g aliquot of dried sample using ethyl acetate/methanol (50:50 %, v/v) as extraction solvent.

Duplicate sample was placed in a 250 ml Erlenmeyer flask, added of 50 ml of extraction solvent, 0.05 ml of internal standard mixtures at 1 µg/ml and then placed in horizontal shaker (speed 10) for 20 minutes.

SLE was repeated three times and the extracts were combined and filtered through a glass-filter frit.

After evaporation to dryness in water-bath at 47°C, the samples were analysed by UHPLC-MS.

2.1.4. Non-processed manure for apolar compounds extraction

Non-processed manure sample (wet weight 500 g) was freeze-dried using Heto DRYWINNER equipment, at -60 °C for two days at about 0.1 mmHg pressure, and then sieved through 2 mm grid.

Solid-Liquid Extraction (SLE) was performed on 1 g aliquot of dried sample using ethyl acetate as extraction solvent.

The sample was placed in a 250 ml Erlenmeyer flask; after addition of 150 ml of ethyl acetate and 0.2 ml of internal standard mixture at 1 µg/ml it was placed in horizontal shaker (speed 10) for 20 minutes.

After shaking, the sample was left to separate into two phases for 30 minutes.

SLE was repeated three times and the extracts were combined and dried onto an anhydrous Na_2SO_4 column previously prepared.

After addition of 0.1 ml of syringe standards mixture at 1 µg/ml, the sample was evaporated to about 0.5 ml volume.

The evaporated extract was finally transferred into a 1.5 ml brown MS vial, using toluene and the final volume adjusted at 0.2 ml, under gentle stream of nitrogen.

2.1.5. Processed manure

Processed manure samples (i.e.: digestate) were filtered through 5 µm and 1 µm glass-fibre disk, consecutively.

Solid and liquid fraction underwent different processing.

Polar compounds were extracted from solid fraction by SLE, using Ethyl Acetate: Methanol 50:50, % v/v as extraction solvent (see Section 2.1.3) and from liquid phase by SPE (see Section 2.1.1).

Apolar substances were extracted from both fractions by solvent extraction using Ethyl Acetate as extraction solvent as reported in Sections 2.1.4 and 2.1.2, respectively.

2.1.6. Soil

Soil samples were freeze-dried using Heto DRYWINNER equipment, at -60°C for two days at about 0.1 mmHg pressure. Before extraction the sample was spiked with 0.2 ml of semi-volatile internal standard mixture at 1 µg/ml and of 0.05 ml of polar internal standards mixture.

50 g of freeze-dried sample were extracted in ultrasonic bath for 30 minutes at 40°C using ethyl acetate and then methanol as extraction solvents. For each solvent, the extraction was repeated three times. Half of the ethyl acetate fraction was used for semi-

volatile analysis. The remaining portion was added to the methanolic fraction and used for polar compounds analysis.

The extracts for semi-volatile analysis were dried onto anhydrous Na_2SO_4 column previously prepared. After addition of 0.1 ml of syringe standards mixture at 1 µg/ml, the samples was evaporated to about 0.5 ml volume, then transferred into a 1.5 ml brown MS vial, using toluene and the final volume adjusted at 0.2 ml, under gentle stream of nitrogen.

The extracts for polar compounds analysis were dried onto anhydrous Na_2SO_4 column previously prepared. After addition of 0.1 ml of syringe standards mixture at 1 µg/ml, the samples was evaporated to about 0.5 ml volume, then transferred into a 1.5 ml brown MS vial, using toluene and the final volume adjusted at 0.2 ml, under gentle stream of nitrogen.

2.1.7. Water for polar and apolar substances

Extraction of water samples were performed using a JRC in-house developed sampling device (i.e.: Mariani box) for on-site Solid Phase Extraction (SPE) of environmental water samples. The procedure is summarised in Table 3 of Annex 1.

HLB SPE Disk (Hydrophilic/Lipophilic Balanced - AtlanticTM HLB-H) filtration/adsorption disks, previously cleaned and conditioned, were used for sample extraction and concentration.

Samples were filtered at an average flow of 0.140 l/min, using the transportable field sampling device developed by JRC (i.e.: Mariani box). Briefly, the device consists of a Teflon holder for the 47mm SPE Disk, a membrane pump, a digital flowmeter counter and a battery (12V-9A/h). All spare parts were assembled in an aluminium box, as depicted in Figure 1.

Figure 1: JRC in-house developed sampling device (i.e.: Mariani box)

The water is sampled from a tube (6) through the pump (4) and organic contaminants are trapped on the filter (1). The flow meter (2, 3) counts the water volume sampled. At the end, the treated water is discharged from tube (7). The pump is powered by a battery (5). The contaminants contained in the filter are further identified and quantified in a specialised laboratory.

HLB disks' activation, drying and elution were performed using an automatic extractor (J2 Scientific).

SPE experimental conditions are summarized in Table 1 of the Annex.

A two fractions sequential elution was performed with 3 x 20 ml ethyl acetate (1st fraction) followed by 3 x 20 ml methanol (2nd fraction). All used solvents were Pesticide Analysis grade.

The ethyl acetate fraction was divided into two portions for the apolar and polar compounds analysis, respectively.

The portion dedicated to apolar analysis was dried onto an anhydrous Na_2SO_4 column previously prepared. After addition of 0.1 ml of syringe standards mixture at 1 µg/ml, the sample was evaporated to about 0.5 ml volume. The evaporated extract was finally transferred into a 1.5 ml brown MS vial, using toluene. The final volume was adjusted at 0.2 ml, under gentle stream of nitrogen and submitted to HRGC-IonTrap-MS analysis.

The portion dedicated to polar compounds analysis was added to the methanolic eluate, mixed and evaporated to dryness.

The sample was reconstituted in 0.5 ml reconstituting solution and analysed by UHPLC-MS/MS.

2.2. Analytical methods

2.2.1. UHPLC-MS/MS

The experimental conditions for polar compounds UHPLC-MSMS analysis are reported in Table 4 in the Annex. The chromatography was performed in gradient mode according to the scheme reported in the Table 5 of the Annex.

2.2.1.1. QTRAP 5500 MS/MS operative conditions

An ABSciex QTRAP5500 mass spectrometer equipped with Turbo V™ ion source was used for polar compounds analysis. The instrument was previously tuned and calibrated in electrospray mode using PPG's. Prior to analysis all the specific parameters were optimized infusing a 1 µg/mL standard solution of analytes and internal standards.

The eluate from the column was introduced directly into the ion source. The rapid desolvatation and vaporization of the droplets minimizes thermal decomposition and preserves their molecular identity.

The data were collected using the software program Analyst 1.6.2.

All calculations were based on chromatographic peak area ratios for the MRM precursor-product ion transitions for analytes versus the relative internal standards.

General operating conditions for QTRAP 5500 MS/MS and parameters of the multi-compound method are reported in Tables 6 of the Annex.

2.2.2. GC-IonTrap-MS

All semi-volatiles pesticides were quantified by isotopic dilution method.

Semi-volatiles pesticides were analysed on HRGC (GC Trace 1310, Thermo Electron, Bremen, Germany), coupled with a ITQ1100 ion-trap mass spectrometer (Thermo Electron, Bremen, Germany) operating in the EI-mode at 70 eV and in scan mode ranging from 50 to 650 m/z.

Pesticides were separated on a 30 m long HP-5ms UI column with 0.25 mm i.d. (inner diameter) and 0.25 µm film (Agilent J&W, USA).

Gas chromatographic conditions were:

PTV injector with temperature program from 100 to 250 °C at 14.5 °C/s, splitless time 1 min., split flow 50 ml/min., constant flow at 1.0 ml min-1 of He, GC-MS interface at 250 °C and a GC program rate: 100 °C for 1 min., 5 °C min-1 to 320 °C for a final isotherm of 3 min.

In Table 8 of the Annex extrapolated mass used for the quantification and retention time for native compounds and internal labelled standards are reported.

2.3. Analytical results

The application of the developed multi-compound methodologies ("*Compound Fishing*") enabled the screening of collected matrices for the presence of about five hundred different chemicals, selected among the main categories of environmental contaminants.

Common processing methods were applied for the extraction of both semi-volatile and polar contaminants, with only mandatory differences due to the chemical nature of contaminants of concern, with the aim of obtaining comparable extracts in terms of presence of interfering substances.

Indeed, the rationale of the new developed processing methods compared to the initial extraction procedures reported as first findings in the Report Part I of pilot sampling campaign (Tavazzi *et al.*, 2018) aimed at improving the experimental conditions for a more effective chemicals extraction. For instance, in the case of urine and liquid manure extraction, SPE was preferred to protein precipitation for its more effective matrix component elimination capabilities.

This screening, being a sort of "chemical fishing" in the multitude of traceable chemicals coming from industry, agriculture and animal husbandry, allowed the identification of the presence of several classes of contaminants. The quantification of identified substances served as a tool for a tentative evaluation of their environmental fate.

Sixty substances out of the about five hundreds listed in Table 1 of the Annex (12%) were above the limit of quantification of the developed procedures and the positive values are reported in the tables hereafter.

The experimental limits of quantification for each substance in every environmental matrix are reported in Tables 9 and 10 of the Annex, for substances detected in GC-IonTrap-MS and LC-MS/MS, respectively. They were calculated considering signal to noise ratio of 10:1.

For the substances which have not been detected in any environmental matrix, the reported LOQ values correspond to the lower level of the calibration curve.

Since concentrations of detected substances in the different environmental matrices have different unit of measurement (i.e.: ng/l and ng/Kg for liquid and solid matrix, respectively), all the values are expressed in the following tables as ppt (part per trillion, 10^{-12}), assuming the density of water, urine and liquid manure is 1 g/ml.

2.3.1. Results of cattle urine analysis

In the analysis of cattle urine samples, four fungicide, two herbicide and two antibiotic residues, belonging to different chemical classes, were detected and quantified.

Azoxystrobin, a systemic fungicide widely used in agriculture providing protection against many types of crops diseases (Catalá-Icardo *et al.*,2017), was found at 7 ppt level.

Two triazole fungicides, tebuconazole and tetraconazole, were detected at 43 and 34 ppt level, respectively.

Thiabendazole, a benzimidazole fungicide and parasiticide able to control helminth species in livestock (EFSA, 2016), was found at 55 ppt level.

Terbutryn, a selective triazine herbicide used both as pre-emergent and post-emergent control agent (Alshallash, 2014), was detected at 32 ppt level.

The urea herbicide Isoproturon was found at 5 ppt level.

The insecticide cypermethrin is widely used to control insects in the household and agricultural fields (Akbar *et al.*, 2015). The compound was measured by GC-IonTrap-MS and detected in urine sample at level near the LOQ value. To better quantify the concentration, the sample was analysed by HRGC-HRMS using the instrumental method described in Mariani *et al.*, 2016. The computed concentration level in the sample was 280 ppt.

The polyether antibiotic monensin, extensively used in dairy to prevent coccidiosis (Watanabe *et al.*, 2008), was detected at 61 ppt level, and the broad-spectrum tetracycline antibiotic, oxytetracycline, used in livestock to correct breathing disorders, was detected at 5191 ppt level. Detailed analytical results are reported in Table 1

Table 1: Results of cattle urine analysis

Analyte	Main category	Category of Use	Concentration (ppt)
Azoxystrobin	Pesticide	Fungicide	6.96
Tebuconazole	Pesticide	Fungicide	43.0
Tetraconazole	Pesticide	Fungicide	33.8
Thiabendazole	Pesticide	Fungicide	55.2
Isoproturon	Pesticide	Herbicide	5.32
Terbutryn	Pesticide	Herbicide	31.7
Cypermethrin (*)	Pesticide	Insecticide	280
Monensin	Pharmaceuticals	Antibiotics	61.1
Oxytetracycline	Pharmaceuticals	Antibiotics	5 191

(*)Cypermethrin concentration value was computed by HRGC-HRMS as described in the text

2.3.2. Results of non-processed manure analysis

Non-processed manure analysis revealed the presence of five residues already detected in cattle urine.

The concentrations of the systemic fungicide azoxystrobin, of the triazole fungicide tebuconazole and of the polyether antibiotic monensin in non-processed manure sample resulted hundreds times higher than in cattle urine, being measured at 7 261, 39 548 and 19 797 ppt level, respectively.

The fungicides tetraconazole and thiabendazole were measured at comparable levels (i.e.: tetraconazole 64 ppt, thiabendazole 10 ppt) than in cattle urine.

Further to the chemical residues already detected and quantified in cattle urine, non-processed manure analysis revealed the presence of three additional compounds.

The azole fungicide cyproconazole, widely used on cereal crops (Saraiva *et al.*, 2018), was found at 270 ppt level; the sulfonamide antimicrobial agent sulfamethazine, usually administered to animals to prevent infectious diseases (Hirth *et al.*, 2016), was found at 407 ppt level; the organic compound piperonyl butoxide, generally used as a component in pesticide formulation and acting as an insecticide synergist by inhibiting the natural defence mechanisms of the insect (Marchand *et al.*, 2017), was found at 4 589 ppt level.

Detailed analytical results of non-processed manure are reported in Table 2.

Table 2: Results of cattle non-processed manure analysis

Analyte	Main category	Category of Use	Concentration (ppt)
Acesulfame K	Personal care	Sweetening agent	167
Azoxystrobin	Pesticide	Fungicide	7 261
Cyproconazole	Pesticide	Fungicide	270
Tebuconazole	Pesticide	Fungicide	39 548
Tetraconazole	Pesticide	Fungicide	63.7
Thiabendazole	Pesticide	Fungicide	9.69
Piperonyl butoxide	Pesticide	Insecticide, synergist	4 589
Monensin	Pharmaceuticals	Antibiotics	19 797
Sulfamethazine	Pharmaceuticals	Antibiotics	407

2.3.3. Results of processed manure analysis

In the analysis of processed manure samples, eleven residues were found, including both compounds already found in either cattle urine or non-processed manure samples and compounds not traceable in the previously mentioned matrices.

Concentration of azoxystrobin and tebuconazole decreased after processing to average values of 437 and 11 534 ppt, respectively, while monensin concentration doubled to about 37 761 ppt.

Both cyproconazole and piperonyl butoxyde concentrations increased to average values of about 18 000 ppt, while Sulfamethazine concentration decreased to about 70 ppt.

Additional residues were found, including the systemic fungicides propiconazole and spiroxamine, detected at average levels of 10 031 and 14 432 ppt, the selective pre-emergent herbicide oxadiazon and the urea herbicide chlorotoluron detected at average levels of 959 and 740 ppt, respectively.

The presence of the sweetening agent acesulfame was detected at 47 405 ppt level.

Results of processed manure samples analysis are reported in Table 3 as sum of concentration found in both solid and liquid fractions. Two samples were collected and their results are reported individually.

Table 3: Results of cattle processed manure analysis

Analyte	Main category	Category of Use	Concentration sample 1 (ppt)	Concentration sample 2 (ppt)
Acesulfame K	Personal care	Sweetening agent	49 362	45 449
Cyproconazole	Pesticide	Fungicide	17 930	18 575
Propiconazole	Pesticide	Fungicide	10 397	9 665
Spiroxamine	Pesticide	Fungicide	16 444	12 421
Azoxystrobin	Pesticide	Fungicide	186	687
Tebuconazole	Pesticide	Fungicide	11 504	11 563
Oxadiazon	Pesticide	Herbicide	1 714	204
Chlorotoluron	Pesticide	Herbicide	648	831
Piperonyl butoxide	Pesticide	Insecticide, synergist	19 150	16 839
Monensin	Pharmaceuticals	Antibiotics	42 836	32 685
Sulfamethazine	Pharmaceuticals	Antibiotics	100	45.6

2.3.4. Results of soil analysis

Soil samples were collected in four different parcels, as indicated in Section 2.2.1 of the Report Part I of pilot sampling campaign (Tavazzi et al., 2018) and analysed.

The analysis of soil samples revealed the presence of thirty one residues, seven of which already found in the previously mentioned matrices.

Azoxystrobin was detected only in soil samples from parcel 2 at 1 400 ppt level; tebuconazole, tetraconazole and thiabendazole concentrations ranged from 15 to 2 353, 145 to 2 301 and from 2 to 39 ppt, respectively.

Cyproconazole and propiconazole were found in all collected parcels and their concentration ranged from 10 to 3 373 and from 45 to 6 166 ppt, respectively.

Cypermethrin, also detected in the cattle urine sample, was found only in soil samples n° 1 and 7 at a concentration level of 15 500 and 75 500 ppt.

Several residues not previously detected, included:

- the bird repellent anthraquinone;
- two pre-emergent soil incorporated herbicides (the chloracetanilide herbicide metolachlor and the dinitroaniline residue, trifluralin);
- three contact and residual herbicides (the chloroacetanilide herbicide metazachlor, the pyridazinone herbicide chloridazon and the urea herbicide chlorotoluron);
- the non-selective herbicide prometon;
- the diacylhidrazine herbicide methoxyfenozide and the benzofuranyl methylcarbamate insecticide furathiocarb;
- six fungicide residues belonging to different chemical classes (boscalid, dimoxystrobin, epoxiconazole, metconazole, hexachlorobenzene and carbendazim)
- the neonicotinoid insecticide imidacloprid;
- the non-systemic pyrethroid insecticide cypermethrin;
- the broad spectrum organophosphate insecticide chlorpyrifos;
- the veterinary antifungal antibiotic flusilazole;
- the obsolete and banned organochlorine insecticides cis-Chlordane and o,p-DDT and p,p'-DDT, together with their breakdown products, p,p'-DDE and p,p' DDD. Concentrations values of the insecticide p,p'-DDT were reformulated according to a corrective factor due to a peak overlap with an unknown co-eluting compound. The two peaks were properly resolved analysing the samples using HRGC-HRMS. The correction procedure is explained in Section 2.4.2. For this reason, p,p'-DDT concentrations should be considered only as indicative of the presence of the compound in soil samples. Detailed analytical results are reported in Table 4.

Table 4: Results of soil analysis

Analyte	Main category	Category of Use	Soil sample (ppt) Parcel 1	Soil sample (ppt) Parcel 2	Soil sample (ppt) Parcel 3	Soil sample (ng/kg) Parcel 7
Anthraquinone	Pesticide	Bird repellent	2215	5660	2464	4797
cis-Chlordane	Pesticide	Insecticide	<LOQ	<LOQ	51	<LOQ
p,p'-DDT	Pesticide	Insecticide	583	830	4579	6536
p,p'-DDE	Pesticide	Breakdown product	1257	1020	2589	1192

Analyte	Main category	Category of Use	Soil sample (ppt) Parcel 1	Soil sample (ppt) Parcel 2	Soil sample (ppt) Parcel 3	Soil sample (ng/kg) Parcel 7
p,p'-DDD	Pesticide	Breakdown product	157	500	2038	1742
Cyproconazole	Pesticide	Fungicide	10	59	82	3373
Propiconazole	Pesticide	Fungicide	45	6166	260	342
Boscalid	Pesticide	Fungicide	865	374	<LOQ	991
Dimoxystrobin	Pesticide	Fungicide	507	141	<LOQ	436
Epoxiconazole	Pesticide	Fungicide	4151	1395	672	6502
Metconazole	Pesticide	Fungicide	<LOQ	184	<LOQ	1622
Tetraconazole	Pesticide	Fungicide	2206	160	145	2301
Azoxystrobin	Pesticide	Fungicide	<LOQ	1400	<LOQ	<LOQ
Tebuconazole	Pesticide	Fungicide	132	22	15	2353
Thiabendazole	Pesticide	Fungicide	2	4	8	39
Hexachlorobenzene	Pesticide	Fungicide	181	198	254	181
Flusilazole	Pesticide	Fungicide	4932	<LOQ	11467	2314
Carbendazim	Pesticide	Fungicide, Breakdown product	102	<LOQ	<LOQ	<LOQ
Metolachlor	Pesticide	Herbicide	108	483	1932	1005
Prometon	Pesticide	Herbicide	23	6	8	9
Chloridazon	Pesticide	Herbicide	1462	1404	802	2905
Chlorotoluron	Pesticide	Herbicide	406	109	7	272
Trifluralin	Pesticide	Herbicide	<LOQ	<LOQ	<LOQ	272
Metazachlor	Pesticide	Herbicide	25478	2661	2454	712356
Methoxyfenozide	Pesticide	Insecticide	24	7194	2271	48
Furathiocarb	Pesticide	Insecticide	17	<LOQ	<LOQ	<LOQ
Imidacloprid	Pesticide	Insecticide	42	<LOQ	<LOQ	61
Cypermethrin	Pesticide	Insecticide	15551	<LOQ	<LOQ	75448
Chlorpyrifos	Pesticide	Insecticide	1509	3493	394	108682
Fluconazole	Pharmaceuticals	Antifungal	<LOQ	<LOQ	3	31

(*) p,p'-DDT concentrations were corrected according to a corrective factor due to a**n** overlap with an unknown compound, as explained in Section 2.4.2

2.3.5. Results of water samples analysis

Environmental water samples collected and analysed included groundwater, run-off and surface waters.

The groundwater sample was collected directly from the well located in the Oponice area.

Three run-off water samples were collected and analysed: one sample was extracted from an irrigation channel flowing between parcels 2 and 3 (i.e.: Run-off water); the other two samples were withdrawn at two different points in an irrigation channel located in parcel 7 (i.e.: Run-off Loc. A and B). Although physically different, these latter two samples are expected to be comparable in terms of possible contamination.

Three surface water samples of Nitra River were collected according to the following scheme:

- one near to pump-house, where river water is collected for irrigation;
- two of them in the dry bed of a Nitra tributary, in the Oponice area, precisely at 25 and 50 meters from the river insertion.

Being the tributary dry in the sampling period, these two latter samples could represent the Nitra River potentially enriched by dry residue coming from the tributary itself.

Forty chemical residues were quantified in water samples, including five chemicals originating from the industrial sector (corrosion inhibitor and surfactants), ten herbicides, eight fungicides and seven insecticides, nine pharmaceuticals and one personal care product.

Detailed analytical results are reported in Table 5.

Table 5: Results of water samples analysis

Analyte	Main category	Category of Use	Ground Water (ppt)	Runoff Water (ppt)	Runnoff. Loc A (ppt)	Runnoff. Loc B (ppt)	Stream oponice 50 m (ppt)	Strem oponice 25 m (ppt)	Nitra River near pumphouse (ppt)
Benzotriazole	Industry	Corrosion Inhibitor	76.9	2.08	2.30	2.77	296	319	220
PFHpA	Industry	Surfactant	1.09	0.434	0.542	0.380	2.07	1.52	0.380
PFHxA	Industry	Surfactant	1.92	1.48	0.946	0.715	2.09	2.40	1.13
PFNA	Industry	Surfactant	0.864	0.290	0.595	0.470	1.41	0.972	0.582
PFOA	Industry	Surfactant	2.14	0.927	0.704	0.937	1.88	1.40	1.23
Acesulfame K	Personal care	Sweetening agent	29.3	26.0	30.4	21.1	31.3	19.5	31.3
Cyproconazole	Pesticide	Fungicide	0.667	1.07	0.664	0.735	1.31	0.970	0.533
Propiconazole	Pesticide	Fungicide	0.837	2.37	1.14	0.830	0.789	2.24	0.842
Azoxystrobin	Pesticide	Fungicide	<LOQ	0.702	0.232	0.152	0.360	0.817	0.242
Epoxiconazole	Pesticide	Fungicide	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.300
Tebuconazole	Pesticide	Fungicide	0.839	1.99	1.66	1.65	2.35	5.61	1.35
Tetraconazole	Pesticide	Fungicide	0.417	<LOQ	0.691	0.328	0.276	0.459	0.066
Thiabendazole	Pesticide	Fungicide	0.234	0.024	0.060	0.070	0.257	0.898	0.513
Tricyclazole	Pesticide	Fungicide	0.064	<LOQ	0.050	0.133	0.076	0.054	0.060
Metolachlor	Pesticide	Herbicide	2.62	27.7	0.874	2.19	5.76	9.00	5.89
2,4,5-T	Pesticide	Herbicide	<LOQ	<LOQ	0.129	<LOQ	0.713	1.13	0.885
2,4-D	Pesticide	Herbicide	1.53	<LOQ	1.04	0.509	3.79	2.15	0.912
Chloridazon	Pesticide	Herbicide	33.7	12.5	6.73	4.01	<LOQ	<LOQ	<LOQ
Chlorotoluron	Pesticide	Herbicide	0.872	1.12	0.876	1.43	3.52	1.65	0.824
Diuron	Pesticide	Herbicide	2.86	0.968	<LOQ	<LOQ	70.4	5.97	7.68
Fluometuron	Pesticide	Herbicide	0.760	0.137	0.750	0.114	5.91	4.22	3.26
Isoproturon	Pesticide	Herbicide	1.41	<LOQ	<LOQ	<LOQ	2.53	<LOQ	<LOQ
Secbumeton	Pesticide	Herbicide	0.061	0.024	<LOQ	<LOQ	0.132	<LOQ	0.072
Terbutryn	Pesticide	Herbicide	0.490	0.180	0.230	0.200	1.11	<LOQ	<LOQ
Chlorpyrifos	Pesticide	Insecticide	19.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Chlothianidin	Pesticide	Insecticide	<LOQ	2.26	<LOQ	<LOQ	2.49	0.990	<LOQ

Analyte	Main category	Category of Use	Ground Water (ppt)	Runoff Water (ppt)	Runnoff. Loc A (ppt)	Runnoff. Loc B (ppt)	Stream oponice 50 m (ppt)	Strem oponice 25 m (ppt)	Nitra River near pumphouse (ppt)
Imidacloprid	Pesticide	Insecticide	0.403	<LOQ	0.191	<LOQ	1.07	0.564	<LOQ
Metaflumizone	Pesticide	Insecticide	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.570	<LOQ
Methoxyfenozide	Pesticide	Insecticide	0.645	35.7	0.893	1.52	0.319	0.336	0.154
Prometryn	Pesticide	Insecticide	0.076	0.066	0.016	<LOQ	0.095	0.113	<LOQ
Piperonyl butoxide	Pesticide	Insecticide, synergist	0.029	<LOQ	0.014	<LOQ	0.161	0.558	0.153
Chlarithromycin	Pharmaceuticals	Antibiotics	<LOQ	<LOQ	<LOQ	<LOQ	32.2	<LOQ	14.3
Monensin	Pharmaceuticals	Antibiotics	0.049	0.078	0.074	0.049	0.264	0.212	0.070
Oxolinic acid	Pharmaceuticals	Antibiotics	1.47	0.143	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Sulfamethazine	Pharmaceuticals	Antibiotics	0.707	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.153
Sulfamethoxazole	Pharmaceuticals	Antibiotics	3.10	0.621	1.22	1.41	7.84	11.0	9.53
Climbazole	Pharmaceuticals	Antifungal	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.65	<LOQ
Fluconazole	Pharmaceuticals	Antifungal	5.10	0.574	1.01	1.06	7.62	7.88	5.57
Diclofenac	Pharmaceuticals	Anti-inflammatory	<LOQ	<LOQ	<LOQ	<LOQ	84.8	193	123
N-Acetyl-Sulfamethoxazole	Pharmaceuticals	Metabolite	<LOQ	<LOQ	<LOQ	<LOQ	6.28	17.7	10.7

2.4. Discussion

2.4.1. Comparison between LC-MS/MS and GC-IonTrap-MS

From the total list of about 500 chemicals, 33 of them have been analysed by both GC-IonTrap-MS and LC-MS/MS methodologies. All of the 33 common chemicals are pesticides.

As reported in Table 6, the majority of common chemicals were found below the LOQ by both techniques. Six out of 33 compounds were only detected by LC-MS/MS, while two of them were detected with both techniques. A single analyte was detected by Ion Trap GC-MS only.

Indeed, the higher sensitivity of LC-MS/MS compared to GC-IonTrap-MS offers the advantage of reaching lower concentration values.

In particular:

- Metolachlor: it was detected in water and soils samples with both techniques. Concentrations in GC-IonTrap-MS were from 1.3 up to 4 times higher than in LC-MS/MS. This substantial difference occurred when measured concentrations were closed to the LOQ of GC-IonTrap-MS method. Concentrations reported in tables referred to LC-MS/MS analysis.
- Tebuconazole: it was detected in water, urine, non-processed manure, processed manure and soil samples by LC-MS/MS. In GC-IonTrap-MS, its presence was observed only in some water samples, but the resulting concentrations were below the LOQ. Concentrations reported in tables referred to LC-MS/MS analysis. Tebuconazole presence in the samples was also confirmed by HRGC-HRMS.
- Flusilazole: comparable concentrations were detected by both analytical techniques. Concentrations reported in tables referred to GC-IonTrap-MS analysis.

Table 6: List of common compound analysed with both analytical methodologies

Compound	GC-IonTrap-MS	LC-MS/MS	Comments
Alachlor	<LOQ	<LOQ	
Atrazine	<LOQ	<LOQ	
Bupirimate	<LOQ	<LOQ	
Carfentrazone ethyl	<LOQ	<LOQ	
Chlorfenvinphos	<LOQ	<LOQ	
Chlorpyrifos	Found in water and soils samples	Not detected	LC-MS Chromatographic failure
Cyprodinil	<LOQ	<LOQ	
Diazinon	<LOQ	<LOQ	
Fenarimol	<LOQ	<LOQ	
Fipronil	<LOQ	<LOQ	

Compound	GC-IonTrap-MS	LC-MS/MS	Comments
Fluquinconazole	<LOQ	<LOQ	
Flusilazole	Found in soil samples	Found in soil samples	Comparable concentrations
Flutolanil	<LOQ	<LOQ	
Flutriafol	<LOQ	<LOQ	
Linuron	<LOQ	<LOQ	
Metalaxyl	<LOQ	<LOQ	
Metolachlor	Found in water and soils samples	Found in water and soil samples	In GC-IonTrap-MS, concentration values are from 1.3 up to 4 times higher than LC-MS/MS
Mevinphos	<LOQ	<LOQ	
Myclobutanil	<LOQ	<LOQ	
Oxadiazon	<LOQ	Found in proc manure samples	
Paclobutrazol	<LOQ	<LOQ	
Penconazole	<LOQ	<LOQ	
Piperonyl butoxide	<LOQ	Found in water, non-processed manure and processed manure samples	
Prochloraz	<LOQ	<LOQ	
Pyridaben	<LOQ	<LOQ	
Pyrimethanil	<LOQ	<LOQ	
Pyriproxyfen	<LOQ	<LOQ	
Tebuconazole	<LOQ	Found in water, urine, non-processed manure, processed manure and soil samples	In GC-IonTrap-MS, only for water samples, a peak is visible, but the computed concentration is <LOQ
Tebufenpyrad	<LOQ	<LOQ	
Triadimefon	<LOQ	<LOQ	

Compound	GC-IonTrap-MS	LC-MS/MS	Comments
Triadimenol	<LOQ	<LOQ	
Tricyclazole	<LOQ	Found in water samples	
Triflumizole	<LOQ	<LOQ	

2.4.2. HRGC-HRMS confirmation analysis of GC-Ion Trap-MS results

In order to confirm the presence of some of the compounds detected by GC-IonTrap-MS, urine, water and soil samples were also qualitatively analysed by HRGC-HRMS. The analysis was done only for specific chemicals under the method discussed in Mariani *et al.*, 2016.

In **urine** samples, the following compounds were identified by HRGC-HRMS:

- Chlorpyrifos (not identified by GC-IonTrap-MS);
- Cypermethrin: for this compound, given the availability of the IS, a quantitative analysis was possible. The concentration value computed by HRGC-HRMS was used in the result table, in place of the values found in GC-IonTrap-MS which was close to the LOQ;
- Endosulphan sulfate (not identified by GC-IonTrap-MS);
- o,p'-DDD(not identified by GC-IonTrap-MS);
- p,p'-DDD (not identified by GC-IonTrap-MS);
- p,p'-DDE (not identified by GC-IonTrap-MS);

In **water** samples, the following compounds were qualitatively identified (not identified by GC-IonTrap-MS, except for one substance in the groundwater sample):

- Chlorphyrifos: in all water samples (identified only in groundwater sample by GC-IonTrap-MS;
- Cypermethryn: in all water samples;
- Beta-HCH: in the groundwater sample and in river samples;
- pp'-DDE: in all water samples;
- Triallate: in river samples
- Trifluralin: very low signal in all water samples;
- Hexachlorobenzene: in all river samples, but also a very low signal in blanks;
- Pentachlorobenzene: in groundwater and all river samples.

In **soil** samples, two of the detected compounds by HRGC-HRMS were also quantified to compare the concentration with the values found by GC-IonTrap-MS:

- Cypermethrin: in soil parcels 1 and 7, as for GC-IonTrap-MS analysis. The compound was also quantified by HRGC-HRMS and concentrations differs for 3% and 14%, respectively for lower and higher concentration;

- Chlorpyrifos: detected and quantified in all samples. The concentration computed by HRGC-HRMS were, in average, 4 times higher than the values obtained by GC-IonTrap-MS;
- Hexachlorobenzene: confirmed in all soil samples;
- Heptachlor epoxide: detected in all soils samples (not identified by Ion trap GC-MS);
- cis-Chlordane: detected in all soil samples (detected by GC-IonTrap-MS in only one soil sample, parcel 3);
- Trifluralin: confirmed in all soil samples;
- DDD: confirmed in all soil samples;
- DDE: confirmed in all soil samples;
- DDT: confirmed in all soil samples. However, its measured concentrations were very high compared to its metabolites, DDE and DDT, supposing, at the beginning, a recent use of DDT. For this reason, a dedicated discussion follows below, with details on p,p'-DDT quantification using a corrective factor.

2.4.3. HRGC-HRMS confirmation analysis of GC-Ion Trap-MS results

As mentioned before, very high suspected concentrations of p,p'-DDT in soils, requested a deeper investigation in order to confirm the results .

A further analysis was carried out by HRGC-HRMS using two capillary columns with different polarity phases:

1. 60 m. long HP-5ms UI column with 0.25 mm i.d. and 0.25 µm film (Agilent J&W, USA);
2. 60 m long HT8 column with 0.25 mm i.d. and 0.25 µm film (SGE Analytical Science, Australia).

In HRGC-HRMS, both columns highlighted two closed but well separated peaks. In Figure 2B, using the HP5 ms column 60 m, a first peak was detected at the retention time (RT) of 20.66 min, which corresponds to p,p'-DDT, and a second peak at RT=20.84 min which is compatible with a different compounds. Similar results were obtained on HT8 column (chromatogram not reported). This suggest the coelution of p,p'-DDT with another chemical with similar mass spectrum, when using a shorter GC column (HP-5 ms, 30 m) on GC-Ion Trap-MS. In Figure 2A, a coeluted peak was detected at the RT of 27.6 min, which correspond to the overlap between p,p'-DDT and the unknown.

In Figure 3A, the mass spectrum of p,p'-DDT is reported; in Figure 3B the mass spectrum of the unknown, detected in soil samples, is given. The two spectra showed a similar pattern, sharing the ions m/z 235 and 237 used for the quantification of DDT. The unknown is characterised by the different ions m/z 164 and 200, instead of ions m/z 165 and 199 which are typical for DDT.

In Figure 4 the list of the first possible candidates for the unknown, extracted from the search tool of the NIST library, is given. Several compounds show a very similar mass spectrum to DDT, having as main masses the ions m/z 235 and 237. However, all listed candidates, missed both the ion m/z 164 and 200 which are typical for the unknown.

Given the existence of a coeluted compound in GC-IonTrap-MS, which interfere with the p,p'-DDT peak, the concentration of p,p'-DDT was corrected using a correction factor. This correction factor (CF) was evaluated for each sample respectively, by computing the ratio between the p,p'-DDT area and the sum of p,p'-DDT and unknown compound areas in the peaks identified in HRGC-HRMS. Then, the area of the peak identified in GC-IonTrap-MS was multiplied by the CF to remove the influence of the coeluted unknown. For this reason, the concentration for the compound p,p'-DDT should be considered as indicative only

Figure 2: p,p'-DDT peak in GC-IonTrap-MS (A, HP-5ms 30 m) and HRGC-HRMS (B, HP-5ms)

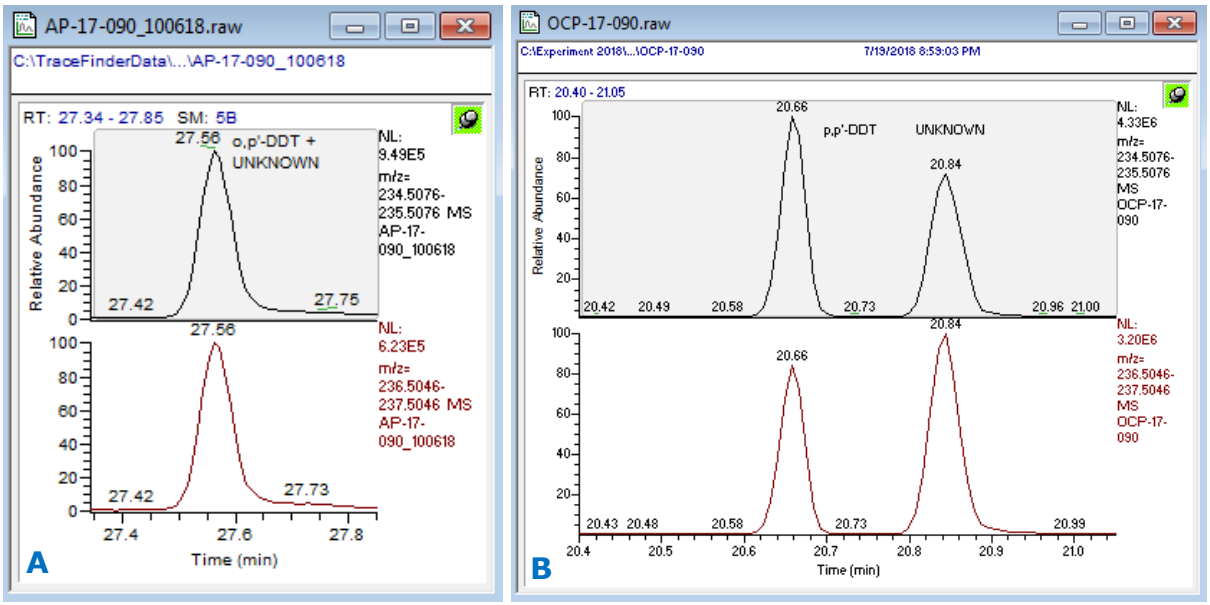


Figure 3: sample spectra of p,p'-DDT (A) and the coeluted unknown (B)

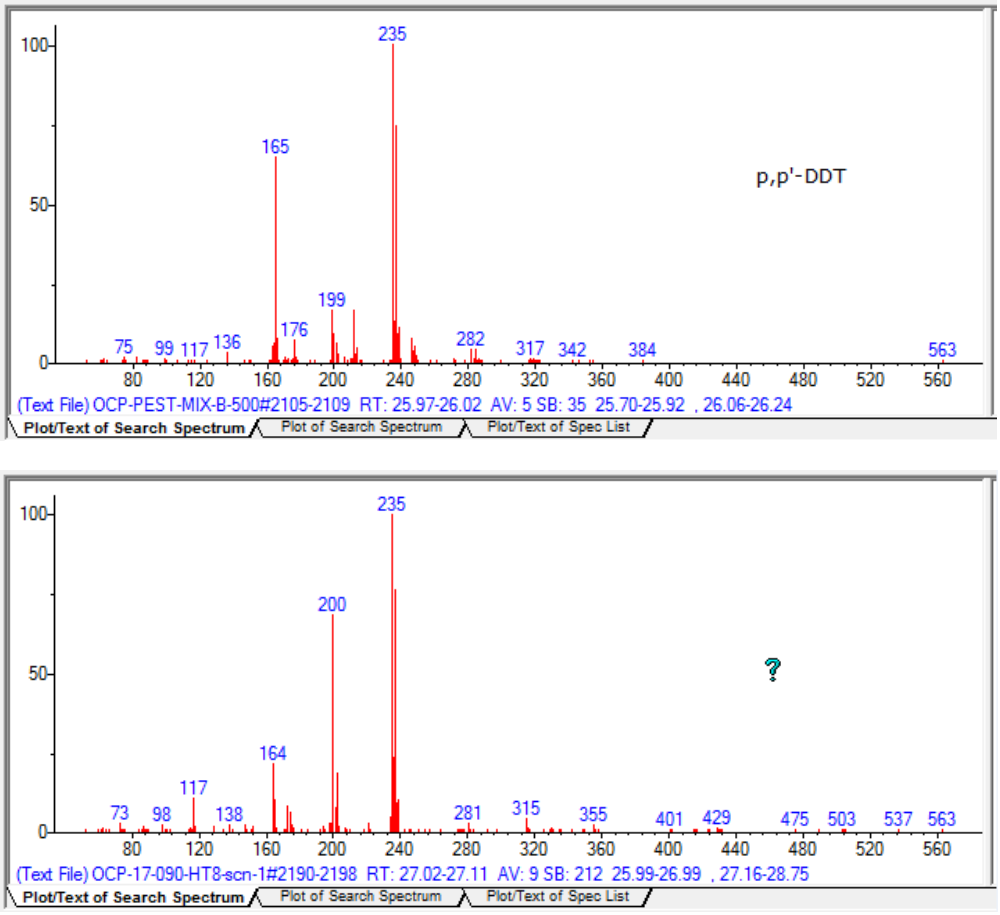
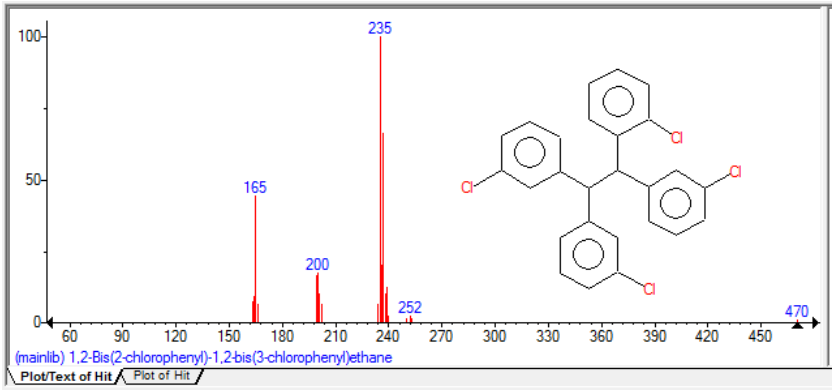
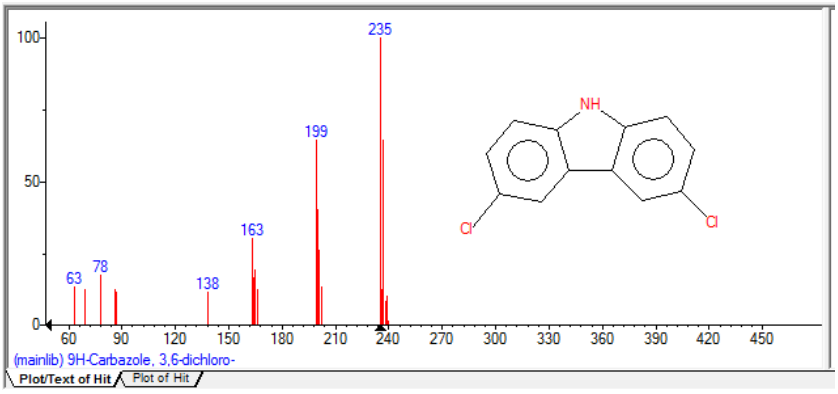
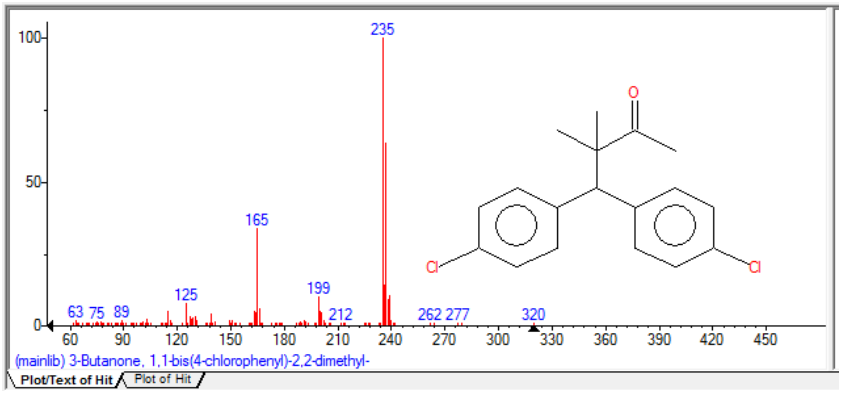
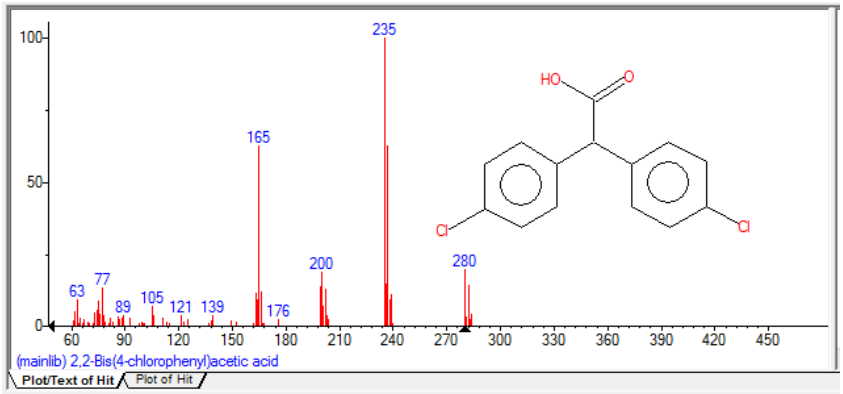


Figure 4: list of possible candidates for the unknown, obtained from the NIST library

Substance name	Library spectra
Name: **1,2-Bis(2.chlorophenyl)-1,2-bis(3-chlorophenyl)ethane** Formula: **C26H18Cl4** Exact mass: **470.016262** Synonyms: **1.1-chloro-2-[1,2,2-tris(3-chlorophenyl)ethyl]benzene**	
Name: **9H-Carbazole, 3,6-dichloro-** Formula: **C12H7Cl2N** Exact mass: **234.995555** Synonyms: **Carbazole, 3,6-dichloro-; 3,6-Dichlorocarbazole**	
Name: **3-Butanone,1,1-bis(4-chlorophenyl)-2,2-dimethyl-** Formula: **C18H18Cl2O** Exact mass: **320.073470** Synonyms: **4,4-Bis(4-chlorophenyl)-3,3-dimethyl-2-butanone**	
Name: **2,2-Bis-(4-chlorophenyl)acetic acid** Formula: **C14H10Cl2O2** Exact mass: **280.005785** Synonyms: **p,p'-DDA; DDA; Dichlorodiphenylacetic acid**	

2.4.4. Observed occurrences and levels

In order to easily summarise, compare and discuss the concentration values found in the different matrices of collected samples, a graphical representation was provided.

Since concentrations of detected compounds in the different environmental matrices have different unit of measurement (i.e.: ng/L and ng/Kg), all the values are expressed in the following charts as ppt (part per trillion, 10^{-12}), assuming the density of water, urine and liquid manure is 1 g/ml.

Concentrations of detected compounds show a huge variation in values (from few ppt to ppb) depending on the type of the measured matrix. In order to represents concentration values, which differs up to 7 orders of magnitude in the same chart, 5 ranges of concentration have been selected. Ranges of concentrations, which are also reported in the legend of each chart, are:

- 0 to 1 ppt
- 1 to 10 ppt
- 10 to 100 ppt
- 100 to 1 000 ppt
- 1 000 to 10 000 ppt
- higher than 10 000 ppt.

Moreover, to condense and make more readable the quantity of information available, some samples were grouped together according to the following computations:

- Processed manure: the concentrations found in the two liquid and solid extracts were summed up to consider the total content in the original manure samples. The two summed samples were then averaged.
- Runoff: samples from location A and B were averaged, since they were collected in the same field
- Non processed manure: the two collected samples, sampled from the same manure batch, were averaged.

Labels for the x-axis of the following charts have been provided according to the matrix of the sample and to the groups of samples described above:

- URINE: cattle urine sample
- MAN: non processed manure samples
- Proc.MAN: processed manure samples;
- SOIL: soil samples. The number indicates the soil parcel;
- RUNOFF: runoff between parcels 2 and 4;
- RUNOFF.AB: two runoff samples from the same parcel 7;
- RIVER.50: surface water at 59 m from the river insertion;
- RIVER.25: surface water at 25 m from the river insertion;
- RIVER: surface water near the pump-house;
- GWW: groundwater sample.

To improve the visualisation of the heterogeneous information, coloured boxes highlight the different matrices involved in the campaign:

- YELLOW: urine samples
- BROWN: manure samples (both processed and non-processed)
- GREEN: soil samples
- BLUE: water samples, including runoff, surface water and groundwater.

The observed occurrences and levels of detected substances are reported in Figure 5 to Figure 10. Hereafter follow a description of the results for each chemical category.

Fungicides (Figure 5)

Five fungicide residues (i.e.: thiabendazole, tetraconazole, tebuconazole, cyproconazole and azoxystrobin) were found in urine, non-processed manure, soil and water samples (even including groundwater). These findings suggest the application of urine and non-processed manure used in agriculture as potential source of environmental contamination. A further fungicide, tricyclazole, was detected in water samples only.

Seven fungicide residues (i.e.: metconazole, hexachlorobenzene, flusilazole, epoxiconazole, dimoxystrobin, carbendazim and boscalid) were found only in soil samples, except epoxiconazole found also in one Nitra river water sample.

Herbicides (Figure 6)

Two herbicides (i.e. isoproturon and terbutryn) were found in urine and some water samples, but not in soil. Prometon and metazachlor were found in soil samples, only, while metolachlor, chlorotoluron and chloridazon were found both in soil and water samples. Five herbicide residues (i.e.: Secbumeton, fluometuron, diuron, 2,4,5-T and 2,4-D) were found in water samples, only.

Insecticides (Figure 7)

Cypermethrin was found in urine and soil samples while piperonyl butoxide was detected in manure and water samples. Methoxyfenozide and imidacloprid were found in soils and waters samples. Chlorpyrifos was found in soil and groundwater.

Furathiocarb was detected only in soil sample from parcel 1. Prometryn and clothianidin were found in waters and metaflumizone only in one river Nitra sample.

Pharmaceuticals & Personal care products (Figure 8)

Oxytetracycline was found in urine sample only. Monensin was found in urine, manure and in all water samples, but not in soils. Sulfamethazine was found in manure, Nitra river and in groundwater samples. Sulfamethoxazole was found in all water samples while its metabolite, N-acetyl-sulfamethoxazole, was detected only in three river samples. Oxolinic acid was detected in run-off and groundwater samples and clarithromycin was found in two river water samples. Two antifungal residues were found: fluconazole was detected in two soil parcels and in all water samples, while climbazole was found only in one Nitra river water sample. The presence of anti-inflammatory drug diclofenac was detected in all three Nitra river water samples. The sweetening agent acesulfame K was detected in manure and all analysed water samples.

Industry (Figure 9)

Four perfluoroalkyl acids (i.e.: perfluorohexanoic acid perfluoroheptanoic acid perfluorooctanoic acid and perfluorononanoic acid) as well as the heterocyclic compound benzotriazole were found in all water samples.

Banned pesticides and bird repellent (Figure 10)

The bird repellent Anthraquinone and background levels of DDTs were found in all soil samples. Very low level of Cis-Chlordane was found in soil sample from parcel 3.

Figure 5: concentrations of fungicides detected in collected samples

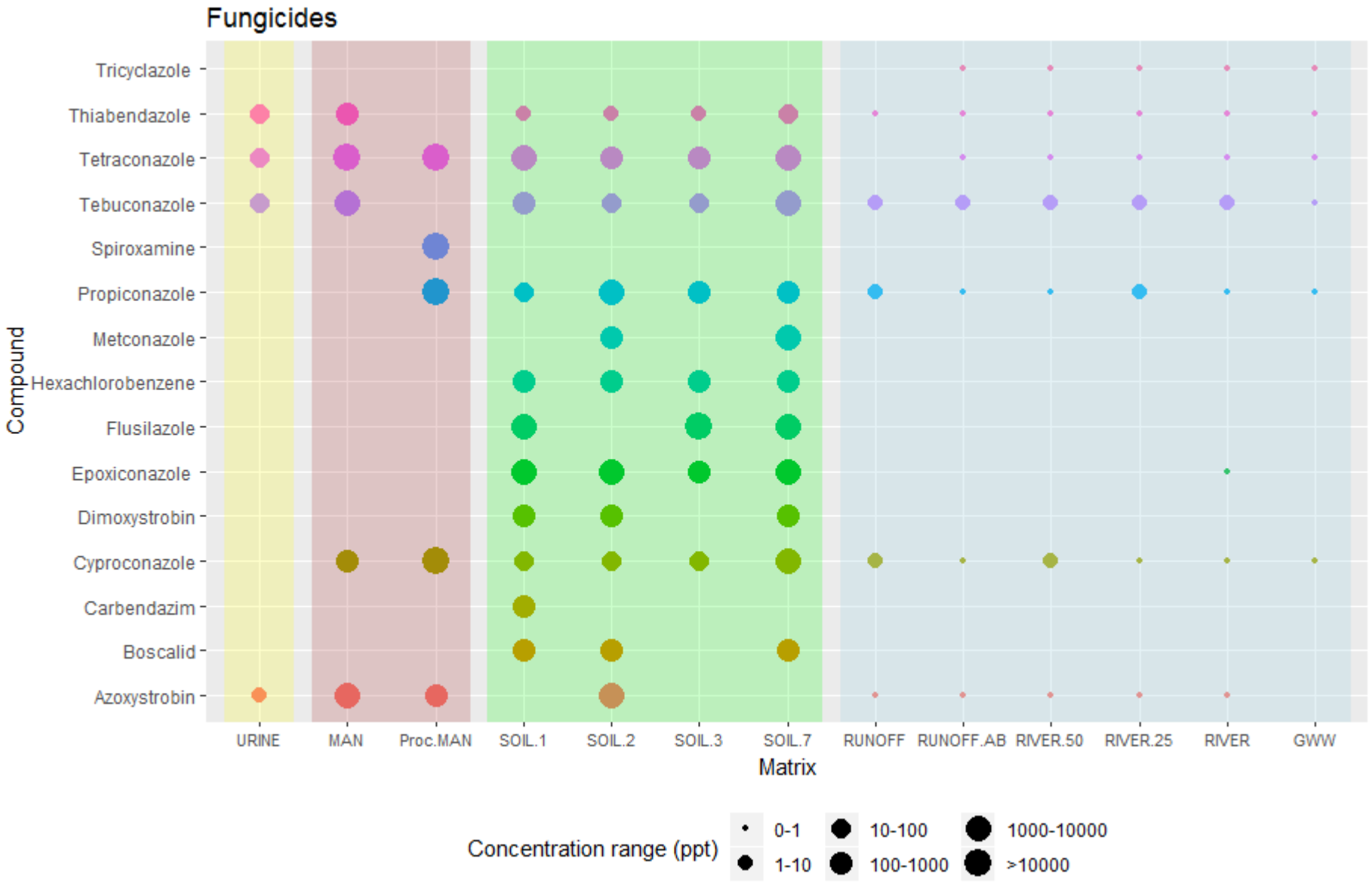


Figure 6: concentrations of herbicides detected in collected samples

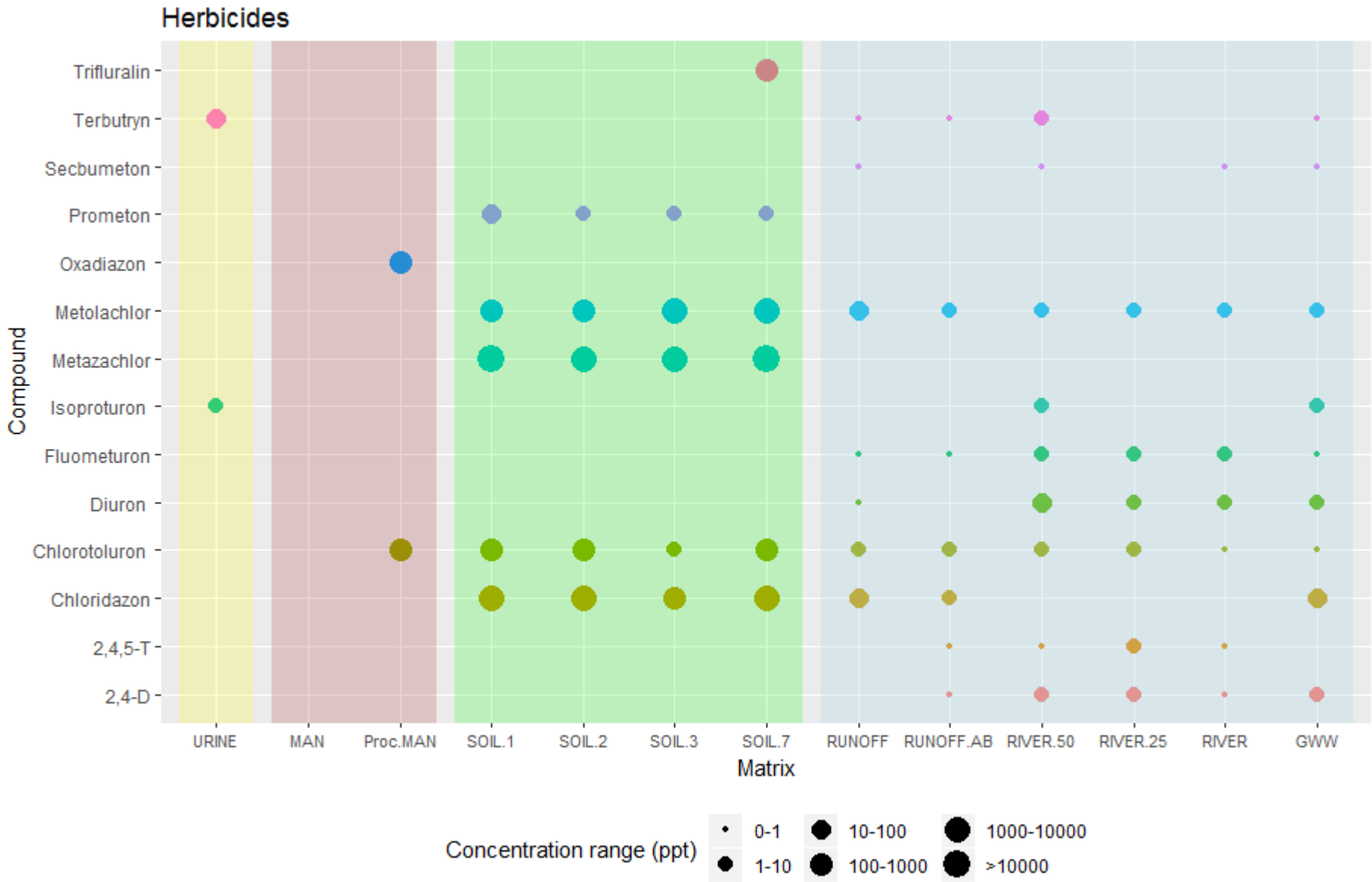


Figure 7: concentrations of insecticides detected in collected samples

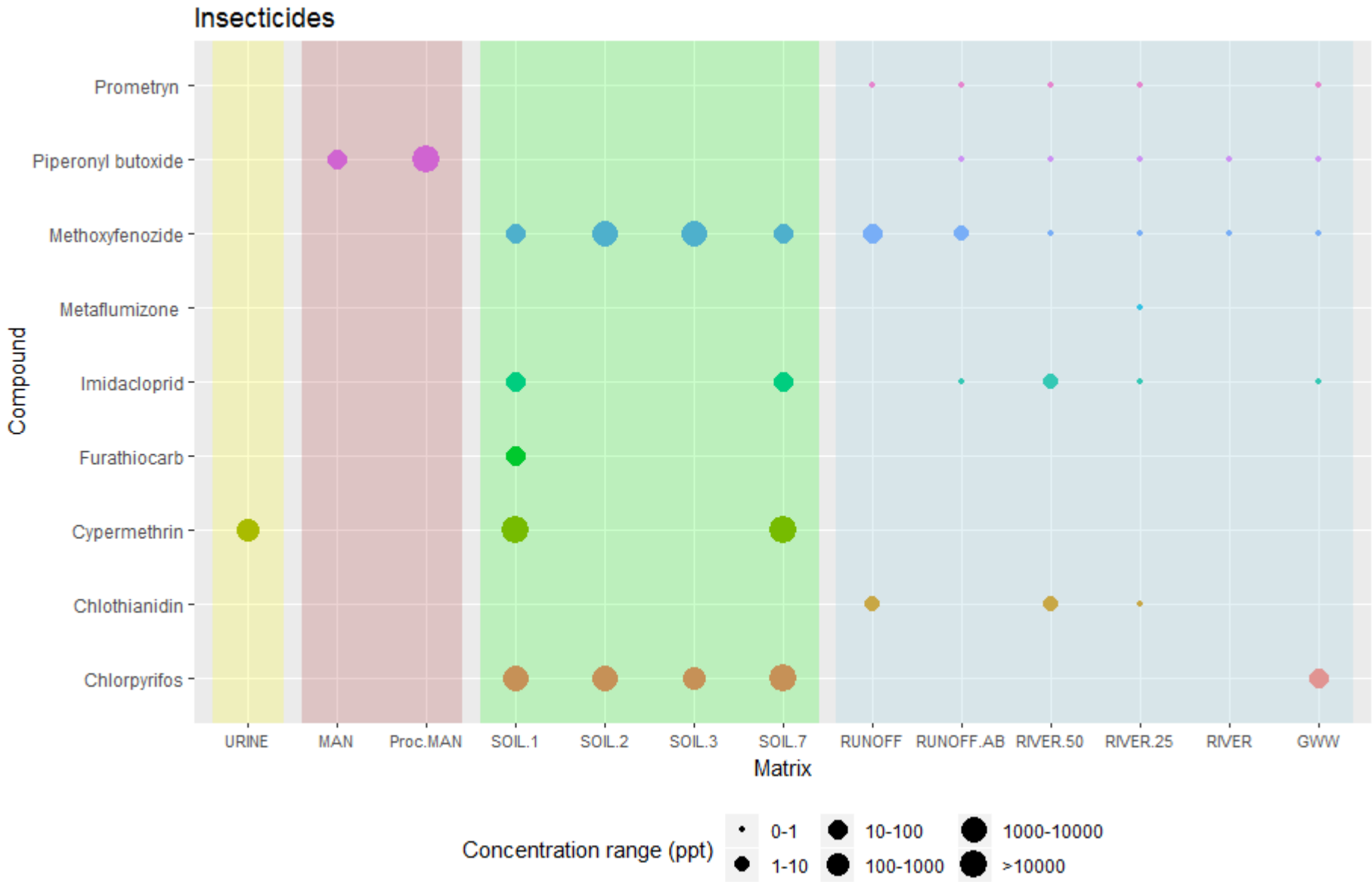


Figure 8: concentrations of pharmaceuticals and personal care products detected in collected samples

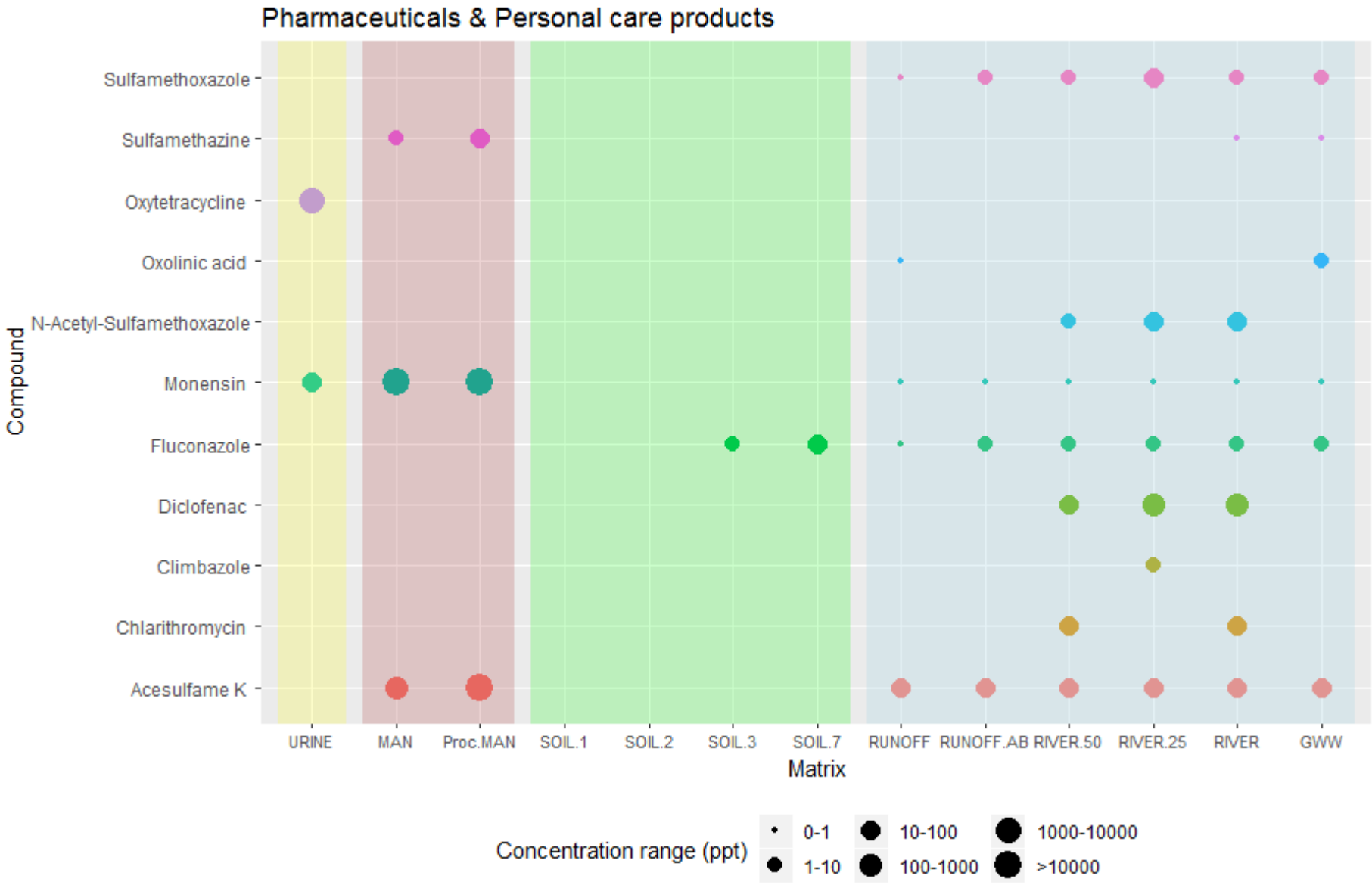


Figure 9: concentrations of industrial products detected in collected samples

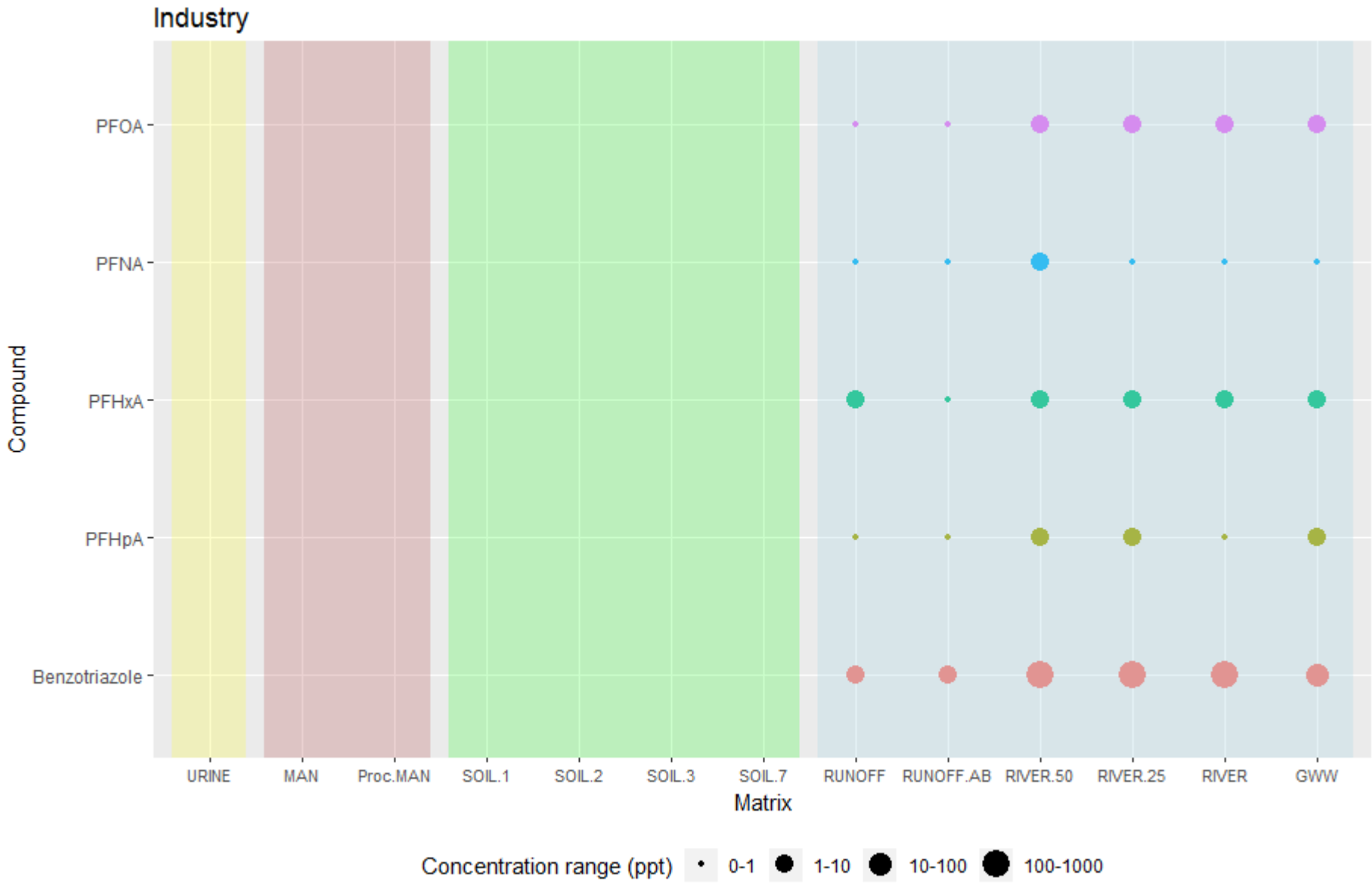
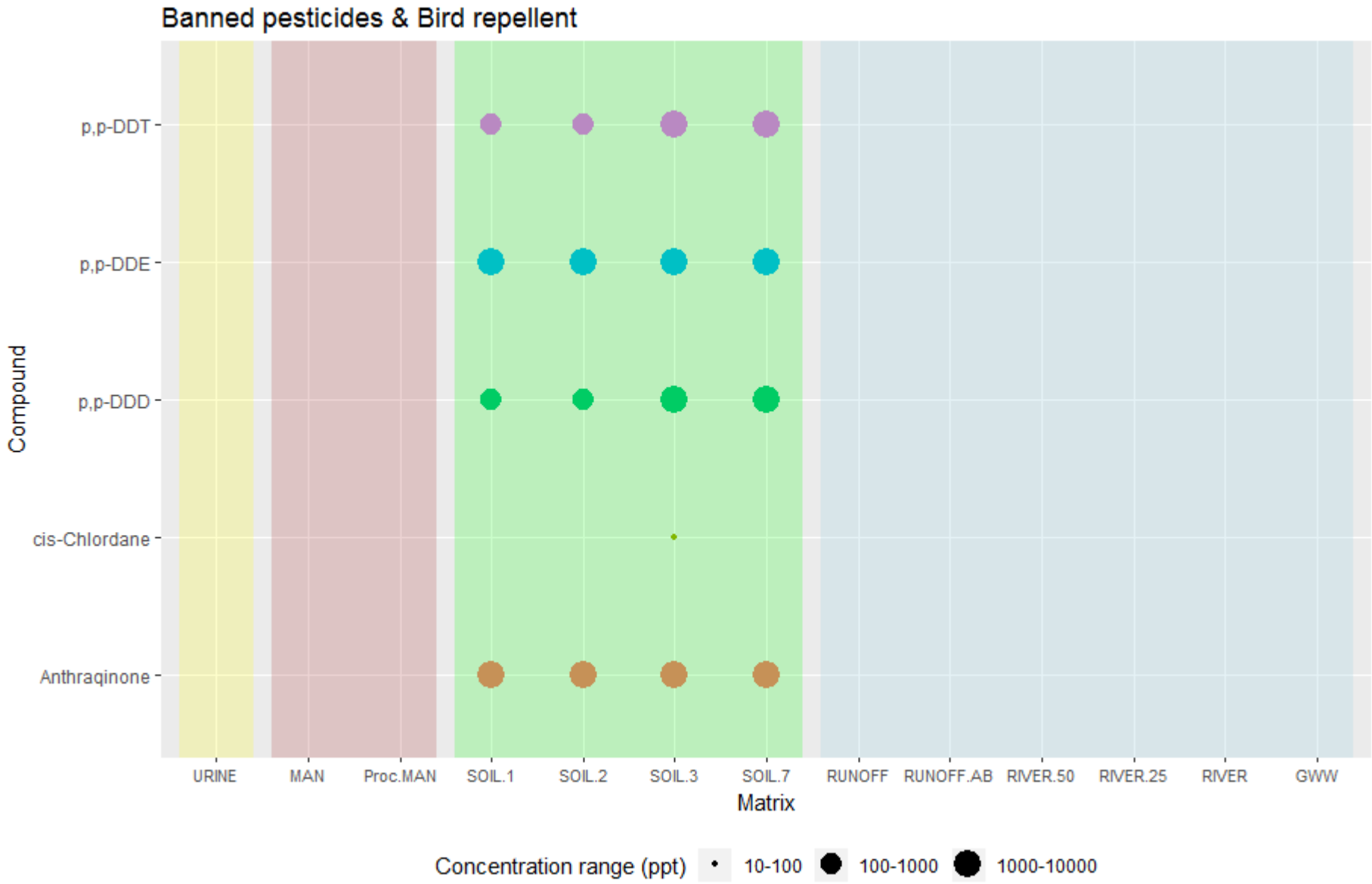


Figure 10: concentrations of banned pesticides and bird repellent detected in collected samples



2.4.5. Qualitative PCA

The application of the principal component analysis (PCA) technique to the dataset, was tentatively done to deduce some additional information. Usually, PCA is carried out to reduce the dimensionality of chemical datasets of different nature, in order to identify potential sources of anthropogenic/natural contamination.

However, to obtain stable results using PCA, the number of samples must be sufficiently greater respect to the number of variables (in this case, variables are the single detected compounds). Moreover, in order to avoid distortion of results, each variable should have a low proportion of data below the limit of detection/quantification.

In this specific case, the number of samples is lower compared to the number of detected compounds and the data below the limit of quantification ranges between 25% and 80%.

A tentative PCA application was however carried out using R software (R version 3.5.0; R Core Team, 2018). Prior to the PCA computation, individual variables measured below quantification limits were replaced by a value closed to zero and a data standardisation procedure was applied in order to avoid the greatest values to have the greatest influence on the analysis.

All single samples were used for the analysis, with an exception for processed manure samples: concentrations in liquid and solid extracts were summed up because the original samples was collected as a mix of solid and liquid manure. It was also decided to remove all detected chemicals stemming from industrial activities, since they were detected in water samples only.

Due to the complexity of different matrices, PCA was applied on separated subsets:

- Water, urine and manure samples;
- Water and soil samples;
- Soil, urine and manure samples.

Results from PCA were quite limitative due to the number of approximations given for the number of samples vs variables, and for the high percentage of concentrations below the limit of quantification. However, two general conclusions resulting from a first analysis, and visualised in PCA charts of Figure 11 and Figure 12, could be drawn:

- Processed manure and non-processed manure were not identified by PCA to have a common origin. Indeed they were collected in different time period and from a different batch of manure and should be treated as different samples;
- Urine and non-processed manure can be treated as a common source for some of the detected compounds.

A further PCA run was then carried out removing processed manure samples from the dataset. This analysis seems to show that the use of urine and manure as fertiliser is a potential source of contamination of waters. The analysis also suggest river water to represent a different group of compounds stemming from other source(s) and/or application(s). In case of soils, PCA analysis did not reveal a particular trend with other matrices, because a lot of pesticides were detected only in soils and thus resulting as a confounding element in PCA analysis.

Figure 11: PCA chart from analysis of manure, soil and urine samples

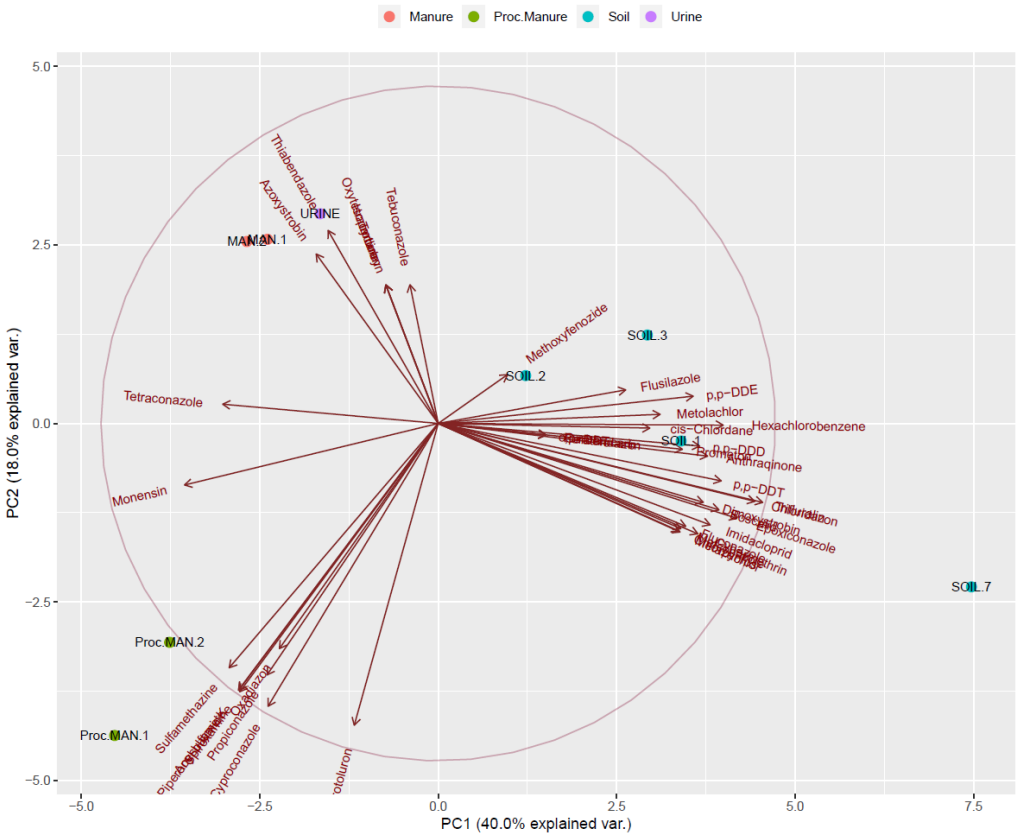
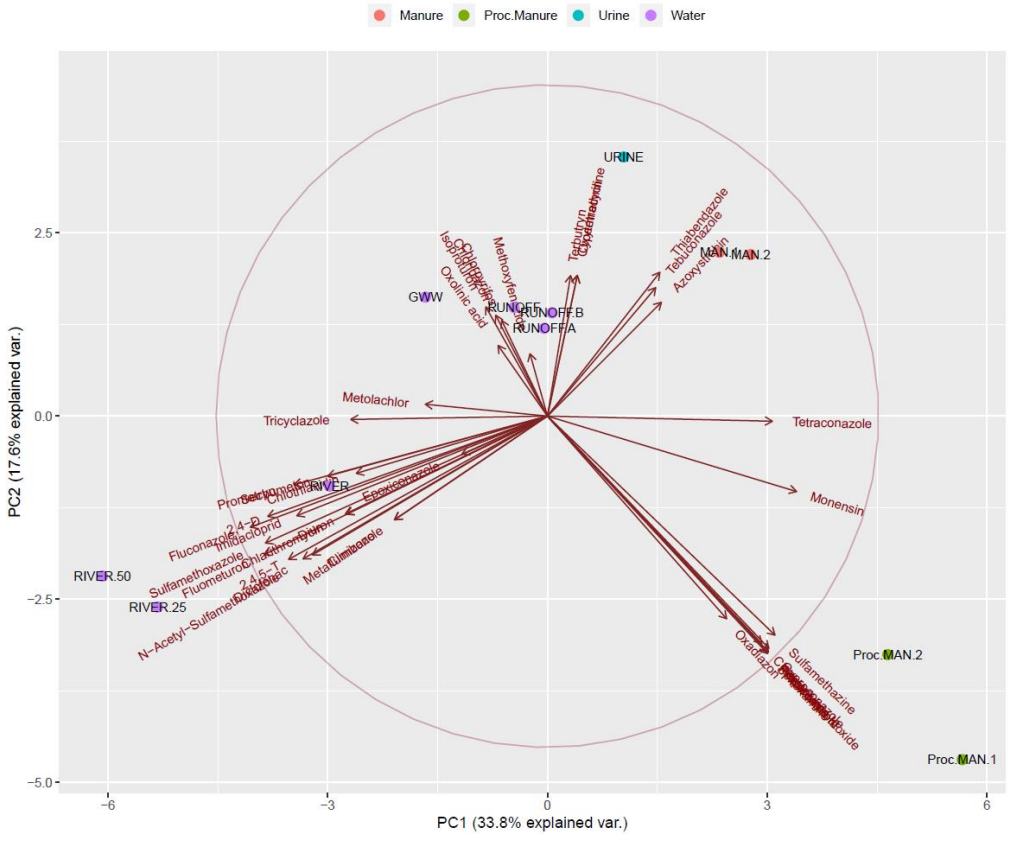


Figure 12: PCA chart from analysis of manure, water and urine samples



3. Design for an EU-wide assessment

The afore-described experiments demonstrate the applicability of what we like to call "*Compound-fishing concept*", i.e. the hybrid approach between a targeted analyses and non-targeted methodologies. The combined assessment of manure, processed manure and exposed water and soil is possible with this methods and can be combined with the assessment of agronomic parameters such as the content of nitrogen and its various forms, the content of phosphorous and other properties relevant to characterise manure and its derived materials as fertilizers.

The relevant environmental processes to be addressed are still complex and it goes without saying that a full experimental characterisation of all processes in all possible cases and scenarios is not possible.

In order to obtain a synergy between the modelling assessments carried out by other groups and the "on site" reality the experimental set-up has to address the following issues regarding the relationship between processed and unprocessed manure materials, their field behaviour in particular also in regard to envisaged definition of safe manure criteria.

3.1. Material characterisation

This includes a direct comparison (where possible) between processed and unprocessed manure. Although, as shown in Figure 13, a variety of processing technologies are known, the focus will be on samples from materials being of interest for a mineral fertiliser equivalence.

In addition to the information retrieved from the providers the following parameters will be tested for:

- Agronomic value:
    - Mineral-N (NH4+, NO3-)
    - Organic nitrogen
    - P-content (and fractionation)
    - K-content
    - Other micro-nutrients
    - Dry-matter content
    - Ash content (loss-on-ignation)

- Environmental risks:
    - Veterinary medicinal agents including antibiotics
    - Pesticides
    - Heavy metals
    - Persistent organic pollutants (Polyaromatic hydrocarbons, poly-chlorinated biphenyls)
    - Others

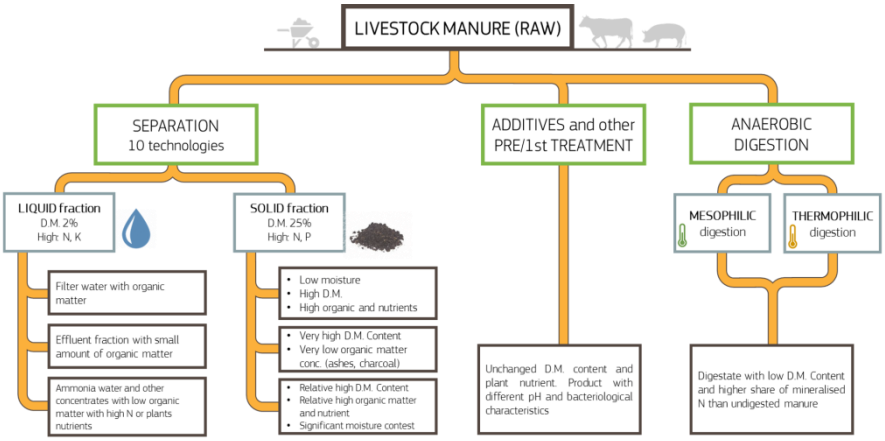
The respective measurements of agronomic value related properties will be outsourced, requiring compliance to ISO 17025 standard and the use of CEN/ISO Standards were applicable.

For the measurement of the organic pollutants the "compound fishing approach" will be used and enlarged to cover some 700 chemical substances. It is expected to perform

these tests on selection of relevant candidate materials and its original manure matrix at a total of ca. 25-30 materials. The candidate materials are currently identified through an open call and will include representatives of all major processing technologies shown in the figure below.

Since the scope of this exercise is NOT to assess the performance of specific manure process plants in terms of variability and homogeneity of the quality of the delivered materials, simple grab samples from the normal production process are sufficient for the scope of the exercise. Generally, sampling approaches should comply with the requirements defined by the Sampling Framework established through CEN TC 292.

Figure 13: Main processing technologies for manure



3.2. Environmental behaviour

Within this framework, the role of agricultural application of manure (processed or not) in the propagation of anti-microbial resistance (AMR), interspecies exchange and antibiotic resistant genes as well as the role of veterinary antimicrobial agents and chemicals related to animal husbandry will be addressed in conjunction with the release of nitrogen species. Indeed, there is a significant data gap on the drainage of nutrients from lands that have been irrigated with treated wastewater or that have been fertilised directly with animal manure or derived biosolids (e.g. after digestion or further processing). Polluted runoff, caused by rainfall, snowmelt or irrigation, moves over and through the ground and carries natural and man-made pollutants that can potentially reach surface water and underground sources of drinking water. This aspect will therefore need to address the seasonality of fertiliser application as well as the different pathways. Although this study does not aim to characterise the respective test sites completely, it will deliver an understanding of environmental pressures created on sites and under real-field scenarios. It is envisaged to perform this in autumn and spring at up to five locations where appropriate candidate materials are used.

4. Conclusions

- The applicability of the novel multi-compound analytical method "*Compound fishing*" as hybrid method, with an analytical performance ranging between and combining the advantages of classical target analysis and non-targeted screening could be demonstrated for the application to manure, treated manure (liquid and solid), soil as well as agricultural runoff, surface and ground water. This allow to better address the so-called "*Circularity of Risks*" stemming from the material reuse and recycling philosophy under a Circular Economy.

- Manure samples (processed and untreated), runoff, groundwater and surface water samples, were analysed for 488 compounds covering typical representatives of herbicides, fungicides, insecticides, pharmaceuticals, ingredients of personal care products and other industrially used chemicals. For 60 of these compounds (corresponding to 12 %), concentration above the established limits of quantification of these novel multi-compound technique were obtained.

- The sampling of environmental water samples (run-off, groundwater and surface water) was successfully done using the MARIANI-Box, thus emphasising once more the validity of the box of environmental organic analyses.

- Matrices derived from animal husbandry contained significant levels of veterinary medicinal agents or chemicals used in animal farming. Quantifiable concentrations were found for:
    - Cattle urine samples for four fungicides, two herbicides and two antibiotic residues
    - Five of the detected residues were also present in the related non-processed manure. In addition acesulfame K as well 3 other substances were identified and quantified
    - The analyses of processed manure revealed the presence of 11 residues, including those found previously. While concentrations of two compounds (azoxystrobin and tebuconazole) decreased, monensin concentration doubled. Although this is no direct proof, it indicates that some compounds may disappear upon treatment of manure, while others persist.
    - The soil measurements revealed – as expected – the presence of significantly larger number of chemicals (in total 31), indicating also that transfer from manure to soil is taking place in some cases.
    - Water samples revealed an even higher number of quantifiable compounds – forty compounds could be identified, which - although not all of them can be linked to manure – proofs a high vulnerability of exposed waters.

- A design for an EU-wide assessment of (processed) manure and an approach to investigate possible transfer pathways for relevant compounds was identified and is put into practice. The exercise will be accompanied by a characterisation of agronomic parameters.

References

Akbar S., Sultan, S., Kertesz M., Determination of Cypermethrin Degradation Potential of Soil Bacteria Along with Plant Growth-Promoting Characteristics, *Current Microbiology*, Vol. 70, 2015, pp. 75-84.

Albero, B., Tadeo, J.L., Escario, M., Miguel, E., Pérez, R.A., Persistence and availability of veterinary antibiotics in soil and soil-manure systems, *Science of The Total Environment*, Vol. 643, 2018, pp. 1562-1570.

Alshallash, K.S., Effect of Pendimethalin, Trifluralin and Terbutryn on Lolium multiflorum growing with barley during pre-emergence stage, *Annals of Agricultural Sciences*, Vol. 59, 2014, pp. 239-242.

Asaduzzaman, M., Antimicrobial resistance: an urgent need for a planetary and ecosystem approach. *The Lancet – Planetary Health 2*, 2018, pp. 99-100.

Berendsen, B.J.A., Lahr, J., Nibbeling, C., Jansen, L.J.M., van de Schans, M.G.M., The persistence of a broad range of antibiotics during calve, pig and broiler manure storage, *Chemosphere*, Vol. 204, 2018, pp. 267-276.

Bottoni, P., Caroli S., Presence of residues and metabolites of pharmaceuticals in environmental compartments, food commodities and workplaces: A review spanning the three-year period 2014–2016, *Microchemical Journal,* Vol. 136, 2018, pp. 2-24.

Bousek, J., Schöpp, T., Schwaiger, B., Lesueur, C., Weissenbacher, N., Behaviour of doxycycline, oxytetracycline, tetracycline and flumequine during manure up-cycling for fertilizer production, *Journal of Environmental Management*, Vol. 223, 2018, pp. 545-553.

Catalá-Icardo, M., Gómez-Benito, C., Simó-Alfonso, E.F., Herrero-Martínez, J.M., Determination of azoxystrobin and chlorothalonil using a methacrylate-based polymer modified with gold nanoparticles as solid-phase extraction sorbent, *Analytical and Bioanalytical Chemistry*, Vol. 409, 2017, pp. 243-250.

Charuaud, L., Jarde, E., Jaffrezic, A., Thomas, M.F., Le Bot, B., Veterinary pharmaceutical residues from natural water to tap water: Sales, occurrence and fate, *Journal of Hazardous Matererials*, Vol. 361, 2019, pp. 169-186.

Chowdhury, R., Sadhukhan, J., Traverso, M., Keen, P.L., Effects of residence time on life cycle assessment of bioenergy production from dairy manure, *Bioresource Technology Reports*, Vol. 4, 2018, pp. 57-65.

Christou, A., Michael, C., Fatta-Kassinos, D., Fotopoulos, V., Can the pharmaceutically active compounds released in agroecosystems be considered as emerging plant stressors?, *Environment International*, Vol. 114, 2018, pp. 360-364.

Conde-Cid, M., Álvarez-Esmorís, C., Paradelo-Núñez, R., Nóvoa-Muñoz, J.C., Arias-Estévez, M., Álvarez-Rodríguez, E., Fernández-Sanjurjo, M.J., Núñez-Delgado, A., Occurrence of tetracyclines and sulfonamides in manures, agricultural soils and crops from different areas in Galicia (NW Spain), *Journal of Cleaner Production*, Vol. 197, 2018, pp. 491-500.

Deng, X.-Y., Gao, K., Addy, M., Li, D., Zhang, R.C., Lu, Q., Ma, Y.-W., Cheng, Y.-L., Chen, P., Liu, Y.-H., Ruan, R., Cultivation of Chlorella vulgaris on anaerobically digested swine manure with daily recycling of the post-harvest culture broth, *Bioresource Technology*, Vol. 247, 2018, pp. 716-723.

De Kraker, M.E.A., Stewardson, A.J., Harbarth, S., Will 10 Million People Die a Year due to Antimicrobial Resistance by 2050? *PLoS Medicine*, Vol. 13, 2016, pp. 1-6.

EFSA (European Food Safety Authority), Revision of the review of the existing maximum residue levels for thiabendazole, *EFSA Journal*, Vol. 14, 2016, doi: 10.2903/j.efsa.2016.4516.

EMA ESVAC (European Medicines Agency, European Surveillance of Veterinary Antimicrobial Consumption), Sales of veterinary antimicrobial agents in 29 EU/EEA countries in 2014 (EMA/61769/2016). Trends from 2011 to 2014. Sixth ESVAC report, 2016.

Ezzariai, A., Hafidi, M., Khadra, A., Aemig, Q., Pinelli, E., Human and veterinary antibiotics during composting of sludge or manure: Global perspectives on persistence, degradation, and resistance genes, *Journal of Hazardous Materials*, Vol. 359, 2018, pp. 465-481.

Fu, S.-F., Chen, K.-Q., Zou, H., Xu, J.-X., Zheng, Y., Wang, Q.-F., Using calcium peroxide (CaO2) as a mediator to accelerate tetracycline removal and improve methane production during co-digestion of corn straw and chicken manure, *Energy Conversion and Management*, Vol. 172, 2018, pp. 588-594.

Grenni, P., Ancona, V., Barra Caracciolo, A., Ecological effects of antibiotics on natural ecosystems: A review, *Microchemical Journal*, Vol. 136, 2018, pp. 25-39.

Hirth, N., Topp, E., Dörfler, U., Stupperich, E., Munch, J.C., Schroll, R., An effective bioremediation approach for enhanced microbial degradation of the veterinary antibiotic sulfamethazine in an agricultural soil, *Chemical and Biological Technologies in Agriculture,* Vol. 3, 2016, pp. 1-11.

Kivits, T., Broers, H.P., Beeltje, H., van Vliet, M., Griffioen, J., Presence and fate of veterinary antibiotics in age-dated groundwater in areas with intensive livestock farming, *Environmental Pollution*, Vol. 241, 2018, pp. 988-998.

Kuppusamy, S., Kakarla, D., Venkateswarlu, K., Megharaj, M., Yoon, Y.-E., Bok Lee, Y., Veterinary antibiotics (VAs) contamination as a global agro-ecological issue: A critical view, *Agriculture, Ecosystems & Environment*, Vol. 257, 2018, pp. 47-59.

Liebig, M., Fernandez, A., Blübaum-Gronau, E., Boxall, A., Brinke, M., Carbonell, G., Egeler, P., Fernandez, C., Fink, G., Garric, J., Halling-Sørense, B., Knacker, T., Krogh, K.A., Küster, A., Löffler, D., Cots, M.A., Pope, L., Prasse, C., Römbke, J., Rönnefahrt, I., Schneider, M.K., Schweitzer, N., Tarazona, J.V., Ternes, T.A., Traunspurger, W., Wehrhan, A., Duis, K., Environmental risk assessment of ivermectin: A case study, *Integrated Environmental Assessment and Management*, Vol. 6, 2010, pp. 567-587.

Liu, N., Han, H., Yin, H., Han, L., Huang, G., Variations in the fate and risk analysis of amoxicillin and its degradation products during pig manure aerobic composting, *Journal of Hazardous Materials*, Vol. 346, 2018, pp. 234-241.

Madikizela, L.M., Ncube, S., Chimuka, L., Uptake of pharmaceuticals by plants grown under hydroponic conditions and natural occurring plant species: A review, *Science of The Total Environment*, Vol. 636, 2018, pp. 477-486.

Marchand, P.A., Dimier-Vallet, C., Vidal, R., Biorational substitution of piperonyl butoxide in organic production: effectiveness of vegetable oils as synergists for pyrethrums, *Environmental Science and Pollution Research*, 2017.

Mariani, G., Tavazzi, S., Skejo, H., Oswald, P., Oleinik, I., Gawlik, B.M., Hanke, G., *EMBLAS II project support activity 2016. Joint Black Sea Survey - Chemical Contaminants. Analytical methodologies and results of ultra-trace organic contaminants monitoring*, Publications Office of the European Union, 2017, Limited dissemination.

Markou, G., Wang, L., Ye, J., Unc, A., Using agro-industrial wastes for the cultivation of microalgae and duckweeds: Contamination risks and biomass safety concerns, *Biotechnology Advances*, Vol. 36, 2018, pp. 1238-1254.

Mullen, R.A., Hurst, J.J., Naas, K.M., Sassoubre, L.M., Aga, D.S., Assessing uptake of antimicrobials by Zea mays L. and prevalence of antimicrobial resistance genes in manure-fertilized soil, *Science of The Total Environment*, Vol. 646, 2019, pp. 409-415.

Pullagurala, V.L.R., Rawat, S., Adisa, I.O., Hernandez-Viezcas, J.A., Peralta-Videa, J.R., Gardea-Torresdey, J.L., Plant uptake and translocation of contaminants of emerging concern in soil, *Science of The Total Environment*, Vol. 636, 2018, pp. 1585-1596.

R Core Team. R: A language and environment for statistical computing. R Foundation for Statistical Computing, 2018, Vienna, Austria. URL https://www.R-project.org/.

Renuka, N., Guldhe, A., Prasanna, R., Singh, P., Bux, F., Microalgae as multi-functional options in modern agriculture: current trends, prospects and challenges, *Biotechnology Advances*, Vol. 36, 2018, pp. 1255-1273.

Riaz, L., Mahmood, T., Khalid, A., Rashid, A., Ahmed Siddique, M.B., Kamal, A., Coyne, M.S., Fluoroquinolones (FQs) in the environment: A review on their abundance, sorption and toxicity in soil, *Chemosphere*, Vol. 191, 2018, pp. 704-720.

Sandoz, M.A., Wooten, K.J., Clendening, S.L., Hensley, L.L., Smith, L.R., Smith, P.N., Transport mechanisms for veterinary pharmaceuticals from beef cattle feedyards to wetlands: Is aerial deposition a contributing source?, *Agriculture, Ecosystems & Environment*, Vol. 252, 2018, pp. 14-21.

Saraiva, A.S., Sarmento, R.A., Golovko, O., Randak, T., Pestana, J.L.T., Soares, A.M.V.M., Lethal and sub-lethal effects of cyproconazole on freshwater organisms: a case study with Chironomus riparius and Dugesia tigrina, *Environmental Science and Pollution Research*, Vol. 25, 2018, 12169-12176.

Sebestyén, I., Monostory, K., Hirka, G., Environmental risk assessment of human and veterinary medicinal products - Challenges and ways of improvement, *Microchemical Journal*, Vol. 136, 2018, pp. 67-70.

Sidhu, H., D'Angelo, E., O'Connor, G., Retention-release of ciprofloxacin and azithromycin in biosolids and biosolids-amended soils, *Science of The Total Environment*, Vol. 650, 2019a, pp.173-183.

Sidhu, H., O'Connor, G., Kruse, J., Plant toxicity and accumulation of biosolids-borne ciprofloxacin and azithromycin, *Science of The Total Environment*, Vol. 648, 2019b, pp. 1219-1226.

Spielmeyer, A., Occurrence and fate of antibiotics in manure during manure treatments: A short review, *Sustainable Chemistry and Pharmacy*, Vol. 9, 2018, pp.76-86.

Stiles, W.A.V., Styles, D., Chapman, S.P., Esteves, S., Bywater, A., Melville, L., Silkina, A., Lupatsch, I., Fuentes Grünewald, C., Lovitt, R., Chaloner, T., Bull, A., Morris, C., Llewellyn, C.A., Using microalgae in the circular economy to valorise anaerobic digestate: challenges and opportunities, *Bioresource Technology*, Vol. 267, 2018, pp. 732-742.

Sui, Q., Meng, X., Wang, R., Zhang, J, Yu, D., Chen, M., Wang, Y., Wei, Y., Effects of endogenous inhibitors on the evolution of antibiotic resistance genes during high solid anaerobic digestion of swine manure, *Bioresource Technology*, Vol. 270, 2018, pp. 328-336.

Tavazzi, S., Mariani, G., Skejø, H., Comero, S., Głowacka, N., Gaduš, J., Gawlik, B.M., *Residues of antimicrobial agents and related compounds of emerging concern in manure, water and soil. Part 1 – Pilot-sampling campaign in Slovakia and first findings*, EUR 29065, Publications Office of the European Union, 2018, doi:10.2760/835417.

Watanabe, N., Harter, T.H., Bergamaschi, B.A., Environmental Occurrence and Shallow Ground Water Detection of the Antibiotic Monensin from Dairy Farms, *Journal of Environmental Quality Abstract - Special Submissions*, Vol. 37, 2008, pp. 78-85.

Zhang, M., He, L.Y., Liu, Y.-S., Zhao, J.-L., Liu, W.-R., Zhang, J.-N., Chen, J., He, L.-K., Zhang, Q.-Q., Ying, G.-G., Fate of veterinary antibiotics during animal manure composting, *Science of The Total Environment*, Vol. 650, 2019, pp. 1363-1370.

List of abbreviations and definitions

AMA	Anti-microbial Agents
AMR	Antimicrobial Resistances
CIAs	Critically Important Antimicrobials
CECs	Compounds of Emerging Concern
CEN	European Committee for Standardization
CF	Correction Factor
EC	European Commission
EFSA	European Food Safety Authority
EI	Electron Ionisation
EMA	European Medicines Agency
ESVAC	European Surveillance of Veterinary Antimicrobial Consumption
EU	European Union
EC	European Commission
GC-MS	Gas Chromatography – Mass Spectrometry
HRGC	High Resolution Gas Chromatography
i.d.	Inner diameter
IS	Internal Standard
ISO	International Organization for Standardization
HLB	Hydrophilic-Lipophilic Balance
JRC	Joint Research Centre
LC-MS/MS	Liquid Chromatography – Mass Spectrometry/Mass Spectrometry
LLE	Liquid–Liquid Extraction
LOQ	Limit of Quantification
MRM	Multiple Reaction Monitoring
MS	Mass Spectrometry
m/z	mass-to-charge ratio
NIST	National Institute of Standards and Technology
PCA	Principal Component Analysis
PCU	Population Correction Unit
PPG	Polypropyleneglycol
ppb	parts per billion
ppt	parts per trillion
PTV	Programmable Temperature Vaporizing
RT	Retention Time
SLE	Solid-Liquid Extraction
SPE	Solid Phase Extraction
UHPLC	Ultra-high-performance liquid chromatography
UI	Ultra Inert
VFA	Volatile Fatty Acids
VMP	Veterinary Medicinal Products
WHO	World Health Organization

Disclaimer

Information regarding typical use categories and fields of application are not specifically referenced in this report and are only for informative purposes. They do not constitute the judgment of the correct use of the substances.

General information on compound use and functions have been retrieved on PubChem, Wikipedia and Chem Portal.

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Annex – Supplementary information

Table A1: Analytes included in the Compound Fishing Method

Analyte ID	Main Category	Sub-Category / Use Type
(Monceren) Pencycuron	Pesticide	Fungicide
10,11-dihydro-10,11-dihydroxy-carbamazepine	Pharmaceuticals	Metabolite
2,3,5,6-Tetrachloroaniline	Pesticide	Metabolite
2,4,5-T	Pesticide	Herbicide
2,4’-DDD	Pesticide	Insecticide, Breakdown product
2,4’-DDE	Pesticide	Breakdown product
2,4’-DDT	Pesticide	Insecticide
2,4’-Methoxychlor	Pesticide	Insecticide
2,4-D	Pesticide	Herbicide
2,6-Dichlorobenzonitrile (Dichlobenil)	Pesticide	Herbicide
2-Phenylphenol	Pesticide	Microbiocide
3,4-Dichloroaniline	Pesticide	Breakdown product
3-Hydroxycarbofuran	Pesticide	Breakdown product
4,4’-DDD	Pesticide	Insecticide, Breakdown product
4,4’-DDE	Pesticide	Breakdown product
4,4’-DDT	Pesticide	Insecticide
4,4’-Methoxychlor olefin	Pesticide	Breakdown product
4-4’-Dichlorobenzophenone	Pesticide	Breakdown product
5-methyl-1H-benzotriazole	Industry	Corrosion inhibitor
Acephate	Pesticide	Insecticide
Acequinocyl	Pesticide	Insecticide
Acesulfame K	Personal Care	Sweetening Agents
Acetamiprid	Pesticide	Neonicotinoid
Acetochlor	Pesticide	Herbicide
Acibenzolar-S-methyl	Pesticide	Fungicide
Aclonifen	Pesticide	Herbicide
Acrinathrin	Pesticide	Insecticide
Alachlor	Pesticide	Herbicide
Alachlor	Pesticide	Herbicide
Alanycarb	Pesticide	Insecticide
Albendazole	Pharmaceuticals	Anthelminthic drug
Albendazole Sulfone	Pharmaceuticals	Metabolite
Albendazole Sulfoxide	Pharmaceuticals	Metabolite
Aldicarb	Pesticide	Insecticide, Nematicide
Aldicarb sulfone	Pesticide	Breakdown product
Aldicarb sulfoxide	Pesticide	Breakdown product
Aldrin	Pesticide	Insecticide
Allidochlor	Pesticide	Herbicide

Analyte ID	Main Category	Sub-Category / Use Type
alpha-BHC	Pesticide	Insecticide
Ametryn	Pesticide	Herbicide
Aminocarb	Pesticide	Insecticide
Amitraz	Pesticide	Insecticide
Amoxicillin	Pharmaceuticals	Antibiotic
Anthraqinone	Pesticide	Bird Repellent
Atrazine	Pesticide	Herbicide
Avermectin B1a	Pesticide	Insecticide
Avermectin B1b	Pesticide	Insecticide
Azinphos ethyl	Pesticide	Insecticide
Azinphos methyl	Pesticide	Insecticide
Azoxystrobin	Pesticide	Fungicide
Azythromycin	Pharmaceuticals	Antibiotic
Benalaxyl	Pesticide	Fungicide
Bendiocarb	Pesticide	Insecticide
Benfluralin	Pesticide	Herbicide
Benfuracarb	Pesticide	Insecticide
Benzotriazole	Industry	Corrosion inhibitor
Benzoximate	Pesticide	Insecticide
beta-BHC	Pesticide	Insecticide
Bezafibrate	Pharmaceuticals	Lipid Regulators
Bifenazate	Pesticide	Insecticide
Bifenthrin	Pesticide	Insecticide
Bioallethrin	Pesticide	Insecticide
Biphenyl	Pesticide	Microbicide, Fungicide
Bitertanol	Pesticide	Fungicide
Boscalid	Pesticide	Fungicide
Bromfenvinfos-methyl	Pesticide	Insecticide
Bromfenvinphos	Pesticide	Insecticide
Bromophos ethyl	Pesticide	Insecticide
Bromophos methyl	Pesticide	Insecticide
Bromopropylate	Pesticide	Insecticide
Bromuconazole Isomer 1	Pesticide	Fungicide
Bromuconazole Isomer 2	Pesticide	Fungicide
Bronopol	Pharmaceuticals	Antibiotics
Bupirimate	Pesticide	Fungicide
Buprofezin	Pesticide	Insect Growth Regulator
Butafenacil	Pesticide	Herbicide
Butocarboxim	Pesticide	Insecticide
Butoxycarboxim	Pesticide	Insecticide
Captafol	Pesticide	Fungicide

Analyte ID	Main Category	Sub-Category / Use Type
Captan	Pesticide	Fungicide
Carbamazepine	Pharmaceuticals	Antiepileptic
Carbaryl	Pesticide	Insecticide, Plant Growth Regulator, Nematicide
Carbendazim	Pesticide	Fungicide, Breakdown product
Carbetamide	Pesticide	Herbicide
Carbofuran	Pesticide	Insecticide, Nematicide
Carbophenothion	Pesticide	Insecticide
Carboxin	Pesticide	Fungicide
Carfentrazone ethyl	Pesticide	Herbicide
Chlorantraniliprole	Pesticide	Insecticide
Chlorbenside	Pesticide	Insecticide
Chlorfenapyr	Pesticide	Insecticide
Chlorfenson (Ovex)	Pesticide	Insect Growth Regulator
Chlorfenvinphos	Pesticide	Insecticide
Chlorfluazuron	Pesticide	Insect Growth Regulator, Insecticide
Chloridazon	Pesticide	Herbicide
Chlorobenzilate	Pesticide	Insecticide
Chloroneb	Pesticide	Fungicide
Chlorotetracyclin	Pharmaceuticals	Antibiotic
Chlorothalonil	Pesticide	Fungicide
Chlorotoluron	Pesticide	Herbicide
Chloroxuron	Pesticide	Herbicide
Chlorpropham	Pesticide	Herbicide, Plant Growth Regulator
Chlorpyrifos	Pesticide	Insecticide, Nematicide
Chlorpyrifos methyl	Pesticide	Insecticide
Chlorthiophos (Isomer I)	Pesticide	Insecticide
Chlorthiophos (Isomer II)	Pesticide	Insecticide
Chlorthiophos (Isomer III)	Pesticide	Insecticide
Chlozolinate	Pesticide	Fungicide
Ciprofloxacin	Pharmaceuticals	Antibiotic
cis-Chlordane	Pesticide	Insecticide
cis-Nonachlor	Pesticide	Insecticide
cis-Permethrin	Pesticide	Insecticide
Clarythromycin	Pharmaceuticals	Antibiotic
Clethodim Isomer 1	Pesticide	Herbicide
Clethodim Isomer 2	Pesticide	Herbicide
Climbazole	Pharmaceuticals	Antifungal
Clofentezine	Pesticide	Insecticide
Clomazone (Command)	Pesticide	Herbicide
Clorpyrifos	Pesticide	Insecticide
Clothianidin	Pesticide	Insecticide

Analyte ID	Main Category	Sub-Category / Use Type
Coumaphos	Pesticide	Insecticide
Cyazofamid	Pesticide	Fungicide
Cybutrine 1	Pesticide	Algaecide, Antifoulant, Breakdown product
Cycloate	Pesticide	Herbicide
Cycluron	Pesticide	Herbicide
Cyfluthrin (Isomer 1)	Pesticide	Insecticide
Cyfluthrin (Isomer 2)	Pesticide	Insecticide
Cyfluthrin (Isomer 3)	Pesticide	Insecticide
Cyfluthrin (Isomer 4)	Pesticide	Insecticide
Cymoxanil	Pesticide	Fungicide
Cypermethrin (Isomer 1)	Pesticide	Insecticide
Cypermethrin (Isomer 2)	Pesticide	Insecticide
Cypermethrin (Isomer 3)	Pesticide	Insecticide
Cypermethrin (Isomer 4)	Pesticide	Insecticide
Cyproconazole Isomer 1	Pesticide	Fungicide
Cyproconazole Isomer 2	Pesticide	Fungicide
Cyprodinil	Pesticide	Fungicide
Cyprodinil	Pesticide	Fungicide
Cyromazine	Pesticide	Insecticide, Insect Growth Regulator
DCPA methyl ester (Chlorthal-dimethyl)	Pesticide	Herbicide
DEET	Pesticide	Insecticide
delta-BHC	Pesticide	Insecticide
Deltamethrin	Pesticide	Insecticide
Desmedipham	Pesticide	Herbicide
Diallate (cis)	Pesticide	Herbicide
Diallate (trans)	Pesticide	Herbicide
Diazinon	Pesticide	Insecticide
Diazinon	Pesticide	Insecticide
Dichlofluanid	Pesticide	Fungicide, Insecticide
Dichloran	Pesticide	Fungicide
Dichlorvos	Pesticide	Insecticide, Breakdown product, Impurity
Diclobutrazol	Pesticide	Fungicide
Diclofenac	Pharmaceuticals	Anti-inflammatory
Dicrotophos	Pesticide	Insecticide
Dieldrin	Pesticide	Insecticide, Breakdown product
Diethofencarb	Pesticide	Fungicide
Difenoconazole Isomer 1	Pesticide	Fungicide
Difenoconazole Isomer 2	Pesticide	Fungicide
Diflubenzuron	Pesticide	Insecticide, Insect Growth Regulator
Dimethachlor	Pesticide	Herbicide
Dimethoate	Pesticide	Insecticide

Analyte ID	Main Category	Sub-Category / Use Type
Dimethomorph Isomer 1	Pesticide	Fungicide
Dimethomorph Isomer 2	Pesticide	Fungicide
Dimoxystrobin	Pesticide	Fungicide
Diniconazole	Pesticide	Fungicide
Dinotefuran	Pesticide	Insecticide
Dioxacarb	Pesticide	Insecticide
Diphenamid	Pesticide	Herbicide
Diphenylamine	Pesticide	Fungicide, Plant Growth Regulator, Insecticide
Disulfoton	Pesticide	Insecticide, Nematicide
Diuron	Pesticide	Herbicide
Doramectin	Pesticide	Acaricide
Edifenphos	Pesticide	Insecticide
Emamectin-benzoate b1a	Pesticide	Insecticide
Emamectin-benzoate b1b	Pesticide	Insecticide
Endosulfan ether	Pesticide	Metabolite
Endosulfan I	Pesticide	Insecticide
Endosulfan II	Pesticide	Insecticide
Endosulfan sulfate	Pesticide	Breakdown product
Endrin	Pesticide	Insecticide, Avicide
Endrin aldehyde	Pesticide	Breakdown product
Endrin ketone	Pesticide	Breakdown product
Enrofloxacin	Pharmaceuticals	Antibiotic
EPN	Pesticide	Insecticide
Epoxiconazole	Pesticide	Fungicide
Eprinomectin	Pesticide	Insecticide
Erythromycin	Pharmaceuticals	Antibiotic
Etaconazole Isomer 1	Pesticide	Fungicide
Etaconazole Isomer 2	Pesticide	Fungicide
Ethafluralin	Pesticide	Herbicide
Ethiofencarb	Pesticide	Insecticide
Ethion	Pesticide	Insecticide
Ethiprole	Pesticide	Insecticide
Ethirimol	Pesticide	Fungicide
Ethofumesate	Pesticide	Herbicide
Ethylan (Penthane)	Pesticide	Insecticide
Etofenprox	Pesticide	Insecticide
Etoxazole	Pesticide	Insecticide
Etridiazole	Pesticide	Fungicide
Famoxadone	Pesticide	Fungicide
Fenamidone	Pesticide	Fungicide
Fenamiphos	Pesticide	Insecticide, Nematicide

Analyte ID	Main Category	Sub-Category / Use Type
Fenarimol	Pesticide	Fungicide
Fenazaquin	Pesticide	Insecticide
Fenbuconazole	Pesticide	Fungicide
Fenchlorphos (Ronnel)	Pesticide	Insecticide
Fenhexamid	Pesticide	Fungicide
Fenitrothion	Pesticide	Insecticide
Fenobucarb	Pesticide	Insecticide
Fenoxycarb	Pesticide	Insecticide, Insect Growth Regulator
Fenpropathrin	Pesticide	Insecticide
Fenpropimorph	Pesticide	Fungicide, Microbiocide
Fenpyroximate	Pesticide	Insecticide
Fenson	Pesticide	Insecticide
Fenthion	Pesticide	Insecticide, Avicide
Fenuron	Pesticide	Herbicide
Fenvalerate (Isomer 1)	Pesticide	Insecticide
Fenvalerate (Isomer 2)	Pesticide	Insecticide
Fipronil	Pesticide	Insecticide
Flochloralin	Pesticide	Herbicide
Flonicamid	Pesticide	Insecticide
Florfenicol	Pharmaceuticals	Antibiotics
Fluazifop-butyl	Pesticide	Herbicide
Fluazinam	Pesticide	Fungicide
Flubendiamide	Pesticide	Insecticide
Fluconazole	Pharmaceuticals	Antifungal
Flucythrinate (Isomer 1)	Pesticide	Insecticide
Flucythrinate (Isomer 2)	Pesticide	Insecticide
Fludioxinil	Pesticide	Herbicide
Flufenacet	Pesticide	Herbicide
Flufenoxuron	Pesticide	Insecticide
Fluometuron	Pesticide	Herbicide
Fluoxastrobin	Pesticide	Fungicide
Fluquinconazole	Pesticide	Fungicide
Fluridone (Sonar)	Pesticide	Herbicide
Flusilazole	Pesticide	Fungicide
Flutolanil	Pesticide	Fungicide
Flutolanil	Pesticide	Fungicide
Flutriafol	Pesticide	Fungicide
Folpet	Pesticide	Fungicide
Fonofos	Pesticide	Insecticide
Forchlorfenuron	Pesticide	Plant Growth Regulator
Formetanate HCl	Pesticide	Insecticide

Analyte ID	Main Category	Sub-Category / Use Type
Fuberidazole	Pesticide	Fungicide
Furalaxyl	Pesticide	Fungicide
Furathiocarb	Pesticide	Insecticide
Gabapentin	Pharmaceuticals	Antiepileptic
gamma-BHC (Lindane)	Pesticide	Insecticide, Rodenticide
Gemfibrozil	Pharmaceuticals	Lipid Regulators
Halofenozide	Pesticide	Insecticide
Heptachlor	Pesticide	Insecticide
Heptachlor epoxide (isomer B)	Pesticide	Breakdown product
Hexachlorobenzene	Pesticide	Microbiocide, Fungicide, Insecticide
Hexaconazole	Pesticide	Fungicide
Hexaflumuron	Pesticide	Insecticide
Hexazinone (Velpar)	Pesticide	Herbicide
Hexythiazox	Pesticide	Insect Growth Regulator
Hydramethylnon	Pesticide	Insecticide
Ibuprofen	Pharmaceuticals	Anti-inflammatory
Imazalil	Pesticide	Fungicide
Imidacloprid	Pesticide	Insecticide
Indoxacarb	Pesticide	Insecticide
Iodofenphos	Pesticide	Insecticide
Ipconazole Isomer 1	Pesticide	Fungicide
Ipconazole Isomer 2	Pesticide	Fungicide
Iprodione	Pesticide	Fungicide
Iprovalicarb Isomer 1	Pesticide	Fungicide
Iprovalicarb Isomer 2	Pesticide	Fungicide
Isazophos	Pesticide	Insecticide
Isocarbophos	Pesticide	Insecticide
Isodrin	Pesticide	Insecticide
Isoprocarb	Pesticide	Insecticide
Isopropalin	Pesticide	Herbicide
Isoproturon	Pesticide	Herbicide
Ivermectin	Pharmaceuticals	Anthelminthic agent
Ketoconazole	Pharmaceuticals	Antifungal
Kresoxim-methyl	Pesticide	Fungicide
lambda-Cyhalothrin	Pesticide	Insecticide
Lenacil	Pesticide	Herbicide
Leptophos	Pesticide	Insecticide
Levamisole	Pharmaceuticals	Anthelminthic drug
Linuron	Pesticide	Herbicide
Lufenuron	Pesticide	Insecticide
Malathion	Pesticide	Insecticide

Analyte ID	Main Category	Sub-Category / Use Type
Mandipropamid	Pesticide	Fungicide
Marbofloxacin	Pharmaceuticals	Antibiotic
MCPA	Pesticide	Herbicide
Mecoprop	Pesticide	Herbicide
Mefenacet	Pesticide	Herbicide
Mepanipyrim	Pesticide	Fungicide
Mepronil	Pesticide	Fungicide
Mesotrione	Pesticide	Herbicide
Metaflumizone	Pesticide	Insecticide
Metalaxyl	Pesticide	Fungicide
Metazachlor	Pesticide	Herbicide
Metconazole	Pesticide	Fungicide
Methabenzthiazuron	Pesticide	Herbicide
Methacrifos	Pesticide	Insecticide
Methamidophos	Pesticide	Insecticide, Breakdown product
Methiocarb	Pesticide	Insecticide, Molluscicide
Methomyl	Pesticide	Insecticide, Breakdown product
Methoprotryne	Pesticide	Herbicide
Methoxychlor	Pesticide	Insecticide
Methoxyfenozide	Pesticide	Insecticide
Methyl parathion	Pesticide	Insecticide, Nematicide
Metobromuron	Pesticide	Herbicide
Metolachlor	Pesticide	Herbicide
Metopropol	Pharmaceuticals	Beta-blocker
Metribuzin	Pesticide	Herbicide
Mevinphos (E isomer)	Pesticide	Insecticide
Mevinphos (Z isomer)	Pesticide	Insecticide
Mevinphos Isomer 1	Pesticide	Insecticide
Mevinphos Isomer 2	Pesticide	Insecticide
Mexacarbate	Pesticide	Insecticide
MGK-264 (Isomer 1)	Pesticide	Synergist
MGK-264 (Isomer 2)	Pesticide	Synergist
Miconazole	Pharmaceuticals	Antifungal
Mirex	Pesticide	Insecticide, Flame retardant
Monensin	Pharmaceuticals	Antibiotic
Monocrotophos	Pesticide	Insecticide
Monolinuron	Pesticide	Herbicide
Moxidectin	Pharmaceuticals	Anthelminthic agent
Myclobutanil	Pesticide	Fungicide
N-(2,4-Dimethylphenyl)formamide	Pesticide	Breakdown product
N-Acetyl-SMZ	Pharmaceuticals	Metabolite

Analyte ID	Main Category	Sub-Category / Use Type
Naproxen	Pharmaceuticals	Anti-inflammatory
Neburon	Pesticide	Herbicide
Nitenpyram	Pesticide	Insecticide
Nitralin	Pesticide	Herbicide
Nitrofen	Pesticide	Herbicide
Norflurazon	Pesticide	Herbicide
Novaluron	Pesticide	Herbicide
Nuarimol	Pesticide	Fungicide
Ofloxacin	Pharmaceuticals	Antibiotic
Omethoate	Pesticide	Insecticide, Breakdown product
Oxadiazon	Pesticide	Herbicide
Oxadixyl	Pesticide	Fungicide
Oxamyl	Pesticide	Insecticide, Nematicide
Oxolinic acid	Pharmaceuticals	Antibiotic
Oxyfluorfen	Pesticide	Herbicide
Oxytetracyclin	Pharmaceuticals	Antibiotic
Paclobutrazol	Pesticide	Plant Growth Regulator
Parathion (ethyl parathion)	Pesticide	Insecticide
Pebulate	Pesticide	Herbicide
Penconazole	Pesticide	Fungicide
Pendimethalin	Pesticide	Herbicide
Pentachloroaniline	Pesticide	Breakdown product
Pentachloroanisole	Pesticide	Metabolite
Pentachlorobenzene	Pesticide	Impurity
Pentachlorobenzonitrile	Pesticide	Fungicides
Pentachloronitrobenzene (quintozene)	Pesticide	Fungicide, Nematicide, Algaecide
Pentachlorothioanisole	Pesticide	Metabolite
PFBA	Industry	non-stick and stain-resistant
PFBS	Industry	
PFHpA	Industry	Breakdown product of stain- and grease-proof coatings on food packaging and household products
PFHxA	Industry	Surfactants
PFHxS	Industry	Surfactants
PFNA	Industry	Fluorosurfactant
PFOA	Industry	Surfactants
PFOS	Industry	Fluorosurfactant
Phenazone	Pharmaceuticals	Analgesic
Phenmedipham	Pesticide	Herbicide
Phenothrin (cis)	Pesticide	Insecticide
Phenothrin (trans)	Pesticide	Insecticide
Phorate	Pesticide	Insecticide, Nematicide

Analyte ID	Main Category	Sub-Category / Use Type
Phosalone	Pesticide	Insecticide
Phosmet	Pesticide	Insecticide
Picoxystrobin	Pesticide	Fungicide
Piperonyl butoxide	Pesticide	Insecticide, Synergist
Pirimicarb	Pesticide	Insecticide
Pirimiphos ethyl	Pesticide	Insecticide
Pirimiphos methyl	Pesticide	Insecticide
Pretilachlor	Pesticide	Herbicide
Prochloraz	Pesticide	Fungicide
Prochloraz	Pesticide	Fungicide
Procymidone	Pesticide	Fungicide
Prodiamine	Pesticide	Herbicide
Profenofos	Pesticide	Insecticide
Profluralin	Pesticide	Herbicide
Promecarb	Pesticide	Insecticide
Prometon	Pesticide	Herbicide
Prometryne	Pesticide	Herbicide
Propachlor	Pesticide	Herbicide
Propamocarb	Pesticide	Fungicide
Propanil	Pesticide	Herbicide
Propargite	Pesticide	Insecticide
Propargite (Isomer 1)	Pesticide	Insecticide
Propargite (Isomer 2)	Pesticide	Insecticide
Propham	Pesticide	Herbicide, Plant Growth Regulator
Propiconazole Isomer 1	Pesticide	Fungicide
Propiconazole Isomer 2	Pesticide	Fungicide
Propisochlor	Pesticide	Herbicide
Propoxur	Pesticide	Insecticide
Propyzamide	Pesticide	Herbicide
Prothioconazole	Pesticide	Fungicide
Prothiofos	Pesticide	Insecticide
Pymetrozine	Pesticide	Insecticide
Pyracarbolid	Pesticide	Fungicide
Pyraclofos	Pesticide	Insecticide
Pyraclostrobin	Pesticide	Fungicide
Pyrazophos	Pesticide	Fungicide
Pyridaben	Pesticide	Insecticide
Pyridafenthion	Pesticide	Insecticide
Pyrimethanil	Pesticide	Fungicide
Pyriproxyfen	Pesticide	Insect Growth Regulator
Quinalphos	Pesticide	Insecticide

Analyte ID	Main Category	Sub-Category / Use Type
Quinmerac	Pesticide	Herbicide
Quinoxyfen	Pesticide	Insecticide
Quinoxyfen	Pesticide	Fungicide
Resmethrin (cis Isomer)	Pesticide	Insecticide
Resmethrin (trans Isomer)	Pesticide	Insecticide
Rotenone	Pesticide	Insecticide
Roxitrhomycin	Pharmaceuticals	Antibiotic
Sarafloxacin	Pharmaceuticals	Antibiotic
Secbumeton	Pesticide	Herbicide
Siduron	Pesticide	Herbicide
Simazine	Pesticide	Herbicide
Simetryn	Pesticide	Herbicide
Spinetoram	Pesticide	Insecticide
Spinosad (Spinosyn A)	Pesticide	Insecticide
Spinosad (Spinosyn D)	Pesticide	Insecticide
Spirodiclofen	Pesticide	Insecticide
Spiromesifen	Pesticide	Insecticide
Spirotetramat	Pesticide	Insecticide
Spiroxamine Isomer 1	Pesticide	Fungicide
Spiroxamine Isomer 2	Pesticide	Fungicide
Streptomycin	Pharmaceuticals	Antibiotic
Sucralose	Personal Care	Sweetening Agents
Sulfadiazine	Pharmaceuticals	Antibiotic
Sulfadimethoxine	Pharmaceuticals	Antibiotic
Sulfamethazine	Pharmaceuticals	Antibiotic
Sulfamethoxazole	Pharmaceuticals	Antibiotic
Sulfathiazole	Pharmaceuticals	Antibiotic
Sulfentrazone	Pesticide	Herbicide
Sulfotepp	Pesticide	Insecticide
Sulprofos	Pesticide	Insecticide
tau-Fluvalinate (Isomer 1)	Pesticide	Insecticide
tau-Fluvalinate (Isomer 2)	Pesticide	Insecticide
Tebuconazole	Pesticide	Fungicide
Tebufenozide	Pesticide	Insecticide
Tebufenpyrad	Pesticide	Insecticide
Tebuthiuron	Pesticide	Herbicide
Teflubenzuron	Pesticide	Insecticide
Tefluthrin	Pesticide	Insecticide
Temephos	Pesticide	Insecticide
Terbacil	Pesticide	Herbicide
Terbufos	Pesticide	Insecticide, Nematicide

Analyte ID	Main Category	Sub-Category / Use Type
Terbumeton	Pesticide	Herbicide
Terbuthylazine	Pesticide	Algaecide, Herbicide, Microbiocide
Terbutryn	Pesticide	Herbicide
Terbutylazine	Pesticide	Herbicide
Tetrachloronitrobenzene (Tecnazene)	Pesticide	Fungicide, Plant Growth Regulator
Tetrachlorvinfos	Pesticide	Insecticide
Tetraconazole	Pesticide	Fungicide
Tetradifon	Pesticide	Insecticide
Tetramethrin (Isomer 1)	Pesticide	Insecticide
Tetramethrin (Isomer 2)	Pesticide	Insecticide
Thiabendazole	Pesticide	Fungicide
Thiacloprid	Pesticide	Insecticide
Thiamethoxam	Pesticide	Insecticide
Thidiazuron	Pesticide	Defoliant, Plant Growth Regulator
Thiobencarb	Pesticide	Herbicide
Thiofanox	Pesticide	Insecticide
Thiophanate-methyl	Pesticide	Fungicide
THPI (Tetrahydrophthalimide)	Pesticide	Breakdown product
Tolclofos-methyl	Pesticide	Fungicide
Toltrazuril	Pharmaceuticals	Coccidiostat
Tolyfluanid	Pesticide	Fungicide, Insecticide
trans-Chlordane	Pesticide	Insecticide
Transfluthrin	Pesticide	Insecticide
trans-Nonachlor	Pesticide	Insecticide
trans-Permethrin	Pesticide	Insecticide
Triadimefon	Pesticide	Fungicide
Triadimenol	Pesticide	Fungicide, Breakdown product
Triallate	Pesticide	Herbicide
Triazophos	Pesticide	Insecticide
Trichlorfon	Pesticide	Insecticide
Tricyclazole	Pesticide	Fungicide
Tricyclazole (Beam)	Pesticide	Fungicide
Trifloxystrobin	Pesticide	Fungicide
Triflumizole	Pesticide	Fungicide
Triflumuron	Pesticide	Insecticide
Trifluralin	Pesticide	Herbicide
Trimethoprim	Pharmaceuticals	Antibiotic
Triticonazole	Pesticide	Fungicide
Vamidothion	Pesticide	Insecticide
Vinclozolin	Pesticide	Fungicide
Zoxamide	Pesticide	Fungicide

Table A2: SPE experimental conditions for HLB cartridge

OASIS HLB cartridge (30 mg, 6cc) cartridge	Volume (ml)	Solvent
Conditioning and pre-cleaning	5	Ethyl acetate
Conditioning and pre-cleaning	5	Methanol
Conditioning	5	Water
Urine sample extraction		
Washing	5	10% Methanol
Drying	Under N2 for 30 min at 20 ml/min	
Elution	6	Ethyl acetate
Elution	6	Methanol

Table A3: SPE experimental conditions for HLB disk

OASIS HLB disk	Volume (ml)	Solvent
Conditioning and pre-cleaning	3 x 20	Ethyl acetate
Conditioning and pre-cleaning	3 x 20	Methanol
Conditioning	1 x 20	Water
Environmental water sample filtration		
Drying	Under N2 for 30 min at 20 ml/min	
Elution	3 x 20	Ethyl acetate
Elution	3 x 20	Methanol

Table A4: UHPLC experimental conditions

Parameter	Type/Values
Pumps	Binary Solvent Manager, Model UPB, Waters (Milford, MA, USA).
Autosampler	Sample Manager, Model UPA, Waters (Milford, MA, USA).
Detector	QTRAP 5500, Applied Biosystems MDS SCIEX, (Foster City, CA, U.S.A) equipped with Turbo V™ ion source.
Flow rate	0.5 ml/min
Injection volume	10 µl
Analytical column	CSH C18 (Thermo), 2.1 x 100 mm, 1.7 µm
Mobile phase	A: 0.1% HCOOH; B: 0.1% HCOOH in MeOH
Reconstituting solution	A:B, 95:5, % v/v

Table A5: UHPLC gradient scheme

Time (min)	Mobile phase (A%)	Mobile Phase B (%)
0	90	10
1.5	90	10
4	40	60
8	30	70
11	0	100
12	0	100
12.1	90	10
15	90	10

Table A6: General operating conditions for QTRAP 5500 MS/MS

Parameter	Value
Scan Type	Scheduled MRM
Polarity	Polarity Switching: Positive/Negative
Ion Source	Turbo Spray
Resolution Q1	Unit
Resolution Q3	Unit
MR Pause	5.0000 msec
Curtain gas (CUR)	25.00
Collision Gas (CAD)	Medium
Temperature (TEM)	550.00
IonSpray Voltage (IS)	± 4 500.00
Ion Source Gas 1 (GS1)	55
Ion Source Gas 2 (GS2)	45
Target Scan Time	0.1 sec
MRM detection window	80 sec

Table A7: MS/MS parameters of the LC multi-compound method

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
329.1	125	6.65	(Monceren) Pencycuron.1	71	10	31	8
329.1	218.1	6.62	(Monceren) Pencycuron.2	71	10	23	14
271	180	3.73	10,11-dihydro-10,11-dihydroxy-carbamazepine	80	10	47	13
271	210	3.73	10,11-dihydro-10,11-dihydroxy-carbamazepine 1	80	10	19	13
271	253	3.73	10,11-dihydro-10,11-dihydroxy-carbamazepine 2	80	10	10	13
255	197	5.7	2,4,5-T	-70	-10	-22	-11
255	161	5.7	2,4,5-T 1	-70	-10	-41	-11

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
219	161	4.91	2,4-D	-130	-10	-24	-11
219	125	4.91	2,4-D 1	-130	-10	-38	-11
225	167	4.91	2,4-D 13C6	-68	-10	-19	-11
238.1	163	3.26	3-Hydroxycarbofuran.1	66	10	19	10
238.1	181	3.26	3-Hydroxycarbofuran.2	66	10	15	12
134	77	0	5-methyl-1H-benzotriazole	260	10	34	13
134	106	0	5-methyl-1H-benzotriazole 1	260	10	23	13
184.1	143	0.67	Acephate.1	46	10	11	28
184.1	49	0.67	Acephate.2	46	10	35	0
162	78	2.92	Acesulfame K	-120	-10	-46	-11
162	82	2.92	Acesulfame K	-120	-10	-27	-11
166	86	2.92	Acesulfame K-D4	-151	-10	-20	-11
166	78	2.92	Acesulfame K-D4	-151	-10	-42	-11
223	126	3.3	Acetamiprid.1	68	10	29	8
223	99	3.36	Acetamiprid.2	68	10	53	6
226	126	3.35	Acetamiprid-d3	80	10	27	13
226	73	3.35	Acetamiprid-d3 1	80	10	80	13
226	190	3.35	Acetamiprid-d3 2	80	10	19	13
211	136.2	4.8	Acibenzolar-S-methyl.1	70	10	41	8
211	91.2	4.8	Acibenzolar-S-methyl.2	70	10	29	4
265.3	248	5.95	Aclonifen	120	10	21	13
265.3	194.1	5.95	Aclonifen 1	120	10	25	13
269.8	253	5.95	Aclonifen D5	120	10	22	13
269.8	186	5.95	Aclonifen D5 1	120	10	40	13
270	238	0.6	Alachlor	120	10	16	13
270	162	0.6	Alachlor	120	10	28	13
283.2	251.1	0.6	Alachlor D13	120	10	15	13
283.2	175.3	0.6	Alachlor D13 1	120	10	26	13
400.1	238.1	5.89	Alanycarb.1	44	10	14	13
400.1	90.9	5.89	Alanycarb.2	44	10	50	4
266.3	234.3	4.13	Albendazole	120	10	30	13
266.3	191	4.13	Albendazole 1	120	10	46	13
266.3	159	4.13	Albendazole 2	120	10	55	13
269.3	234.2	4.13	Albendazole D3	100	10	27	13
269.3	191.2	4.13	Albendazole D3 1	100	10	45	13
269.3	159.3	4.13	Albendazole D3 2	100	10	51	13
298	159	0	Albendazole Sulfone	280	10	50	13
298	104	0	Albendazole Sulfone 1	280	10	76	13
282	208	0	Albendazole Sulfoxide	100	10	32	13
282	191	0	Albendazole Sulfoxide 1	100	10	51	13
240.1	86.2	1.42	Aldicarb sulfone.1	28	10	28	4
240.1	148.2	1.42	Aldicarb sulfone.2	28	10	19	10
207.1	132.1	1.16	Aldicarb sulfoxide.1	56	10	9	8
207.1	89.1	1.16	Aldicarb sulfoxide.2	56	10	19	6

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
208.1	116	1.42	Aldicarb.1	26	10	11	6
208.1	89	1.42	Aldicarb.2	26	10	23	4
228.1	186.1	3.83	Ametryn.1	65	10	25	12
228.1	96	3.83	Ametryn.2	65	10	35	6
209.1	137.1	0.39	Aminocarb.1	56	10	33	8
209.1	152	0.39	Aminocarb.2	56	10	19	10
294.2	148.3	5.85	Amitraz.1	98	10	22	9
294.2	91.2	5.85	Amitraz.2	98	10	57	5
366.3	349.3	0	Amoxicillin	70	10	10	13
366.3	113.8	0	Amoxicillin 1	70	10	30	13
366.3	134.2	0	Amoxicillin 2	70	10	45	13
216	174	4.48	Atrazine	258	10	25	13
216	104	4.48	Atrazine	258	10	40	13
219	177	4.48	Atrazine 13C3	100	10	25	13
890.5	567.5	10.12	Avermectin B1a.1	61	10	17	18
890.5	305	10.12	Avermectin B1a.2	61	10	35	8
876.5	553.4	9.9	Avermectin B1b.1	61	10	17	16
876.5	291	9.9	Avermectin B1b.2	61	10	29	20
404.1	372.1	4.79	Azoxystrobin.1	65	10	19	10
404.1	344.1	4.79	Azoxystrobin.2	65	10	33	10
749.6	591.4	3.07	Azythromycin	200	10	40	13
749.6	573.3	3.07	Azythromycin 1	200	10	47	13
326.2	294.1	5.85	Benalaxyl.1	60	10	15	8
326.2	148.1	5.85	Benalaxyl.2	60	10	29	8
224.1	167.1	4.03	Bendiocarb.1	61	10	15	10
224.1	109	4.03	Bendiocarb.2	61	10	33	6
411.2	190	0	Benfuracarb.1	34	10	15	9
411.2	252.1	0	Benfuracarb.2	36	10	17	8
120	65	2.5	Benzotriazole	209	10	29	13
120	92	2.5	Benzotriazole 1	209	10	24	13
124	69	2.5	Benzotriazole d4	56	10	35	13
364	199	6.4	Benzoximate.1	31	10	11	12
364	105	6.4	Benzoximate.2	31	10	31	6
360	274	5.15	Bezafibrate	-100	-10	-24	-11
360	154	5.15	Bezafibrate	-100	-10	-39	-11
364	278	5.15	Bezafibrate D4	-165	-10	-24	-11
301.1	170.1	5.18	Bifenazate.1	66	10	27	10
301.1	198.1	5.18	Bifenazate.2	66	10	13	12
346.3	314	0	Bifenox D3	80	10	12	13
338.2	269.2	6.44	Bitertanol.1	56	10	13	2
338.2	70	6.44	Bitertanol.2	56	10	29	12
343	307	4.98	Boscalid.1	35	10	27	8
343	140	4.98	Boscalid.2	35	10	25	8
378	159	5.08	Bromucanozole Isomer 1.1*	46	10	37	2

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
378	70	5.08	Bromucanozole Isomer 1.2*	46	10	47	6
378.001	159	5.08	Bromucanozole Isomer 2.1*	46	10	37	2
378.001	70	5.08	Bromucanozole Isomer 2.2*	46	10	47	6
199	155	0.6	Bronopol	-100	-10	-20	-11
199	181	0.6	Bronopol 1	-100	-10	-15	-11
199	80	0.6	Bronopol 2	-100	-10	-50	-11
317	166.1	4.6	Bupirimate.1	91	10	33	10
317	108	4.6	Bupirimate.2	91	10	35	6
306.2	201.1	6.35	Buprofezin.1	56	10	17	12
306.2	116.2	6.35	Buprofezin.2	36	10	23	6
492.1	331	5.27	Butafenacil.1	68	10	27	8
492.1	349	5.27	Butafenacil.2	68	10	19	10
213.1	75.1	3.61	Butocarboxim.1	86	10	19	3
213.1	116	3.61	Butocarboxim.2	86	10	17	6
223.1	106	1.35	Butoxycarboxim.1	61	10	13	6
223.1	166	1.35	Butoxycarboxim.2	61	10	11	10
198	140	0	Caffeine 13C3	150	10	27	13
198	112	0	Caffeine 13C31	150	10	33	13
237	194	4.3	Carbamazepine	250	10	28	13
237	165	4.3	Carbamazepine	250	10	60	13
247	204	4.3	Carbamazepine d10	234	10	31	13
202.1	145	4.22	Carbaryl.1	51	10	13	8
202.1	127	4.22	Carbaryl.2	51	10	39	32
192.2	160.2	0.77	Carbendazim.1	61	10	25	10
192.2	132.1	0.77	Carbendazim.2	61	10	41	8
237.1	192	3.85	Carbetamide.1	56	10	13	12
237.1	118.1	3.85	Carbetamide.2	56	10	17	6
222.1	165.1	4.03	Carbofuran.1	65	10	17	10
222.1	123	4.03	Carbofuran.2	65	10	29	8
236.1	143	4.22	Carboxin.1	66	10	21	8
236.1	87	4.22	Carboxin.2	66	10	33	6
412	346	5.75	Carfentrazone-ethyl.1	91	10	31	6
412	366	5.75	Carfentrazone-ethyl.2	91	10	25	10
484	452.9	4.7	Chlorantraniliprole.1	61	10	21	12
484	285.9	4.7	Chlorantraniliprole.2	61	10	17	8
359	99	6.15	Chlorfenvinphos	100	10	46	13
359	170	6.15	Chlorfenvinphos 1	100	10	55	13
369	205	6.15	Chlorfenvinphos D10	100	10	30	13
369	133	6.15	Chlorfenvinphos D10 1	100	10	25	13
540	383	9.82	Chlorfluazuron.1	93	10	27	10
540	158	9.82	Chlorfluazuron.2	93	10	29	10
222	77	3.3	Chloridazon	204	10	52	13
222	65	3.3	Chloridazon 1	204	10	53	13
222	92	3.3	Chloridazon 2	204	10	34	13

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
479.2	444	3	Chlorotetracyclin	80	10	23	13
479.2	462.3	3	Chlorotetracyclin 1	80	10	23	13
479.2	139	3	Chlorotetracyclin 2	80	10	137	13
213.1	72.2	4.42	Chlorotoluron.1	68	10	31	4
213.1	46.2	4.42	Chlorotoluron.2	68	10	35	8
291.1	72.4	5.24	Chloroxuron.1	81	10	47	4
291.1	218.1	5.24	Chloroxuron.2	81	10	33	14
350.6	197.8	8.42	Chlorpyrifos 1	80	10	29	13
360.1	199	8.42	Chlorpyrifos D10	100	10	29	13
360.1	107	8.42	Chlorpyrifos D10 1	100	10	80	13
332	231	0	Ciprofloxacin	290	10	37	13
332	314	0	Ciprofloxacin	290	10	25	13
336	235	0	Ciprofloxacin 13C3	239	10	51	13
336	291	0	Ciprofloxacin 13C3 1	239	10	25	13
748.5	590.5	4.36	Clarythromycin	100	10	28	13
748.5	558.5	4.36	Clarythromycin 1	100	10	31	13
360.1	164	5.18	Clethodim Isomer 1.1*	51	10	29	10
360.1	268.1	5.18	Clethodim Isomer 1.2*	51	10	17	18
360.101	164	7.19	Clethodim Isomer 2.1*	51	10	29	10
360.101	268.1	7.19	Clethodim Isomer 2.2*	51	10	17	18
293	69	3.9	Climbazole	90	10	27	13
293	99	3.9	Climbazole 2	90	10	63	13
297	201.2	3.9	Climbazole D4	80	10	42	13
297	102.8	3.9	Climbazole D4 1	80	10	64	13
303	138	6.42	Clofentezine.1	56	10	19	8
303	102	6.42	Clofentezine.2	56	10	51	6
350.6	96.8	8.42	Clorpyrifos	80	10	45	13
250	169	3.07	Clothianidin.1	56	10	19	10
250	132	3.07	Clothianidin.2	56	10	21	8
253	172	3.12	Clothianidin-d3 1	50	10	18	13
325.2	108	5.56	Cyazofamid.1	50	10	18	6
325.2	261.2	5.56	Cyazofamid.2	50	10	14	6
254	198	4.5	Cybutrine 1	261	10	26	13
263	74	4.5	Cybutrine d9 1	269	10	61	13
263	199	4.5	Cybutryine d9	269	10	27	13
254	74	4.5	Cybutryne 2	261	10	30	13
199.1	89.1	4.51	Cycluron.1	71	10	21	4
199.1	89	4.51	Cycluron.2	71	10	21	6
198.9	128.2	3.36	Cymoxanil.1	56	10	12	7
198.9	111.2	3.36	Cymoxanil.2	56	10	23	6
292	70	5.12	Cyproconazole Isomer 1.2*	66	10	31	2
292	125	5.12	Cyproconazole Isomer 1.2*	66	10	29	10
292.001	70	5.29	Cyproconazole Isomer 2.1*	66	10	31	2

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
292.001	125	5.29	Cyproconazole Isomer 2.2*	66	10	29	10
226	93	4.51	Cyprodinil.1	91	10	47	6
226	77	4.51	Cyprodinil.2	91	10	61	4
167.1	85.1	0.29	Cyromazine.1	89	10	26	4
167.1	125.1	0.29	Cyromazine.2	89	10	24	7
192	91	4.52	DEET	244	10	41	13
192	119	4.52	DEET	244	10	24	13
198	91	4.52	DEET d6	80	10	42	13
318.1	182	4.7	Desmedipham.1	36	10	19	12
318.1	154	4.7	Desmedipham.2	36	10	35	26
305	159	5.9	Diazinon	100	10	30	13
305	97	5.9	Diazinon 1	100	10	55	13
315.3	170	5.9	Diazinon D10	70	10	35	13
315.3	154.2	5.9	Diazinon D10 1	100	10	5	13
221.9	109	4	Dichlorvos	100	10	25	13
221.9	95	4	Dichlorvos 1	100	10	50	13
227	115	4	Dichlorvos D6	100	10	26	13
227	83	4	Dichlorvos D6 1	100	10	37	13
328.2	70.2	5.9	Diclobutrazol.1	70	10	48	3
328.2	59.1	5.8	Diclobutrazol.2	70	10	48	2
294	250	6.14	Diclofenac	-42	-10	-16	-11
294	214	6.14	Diclofenac	-42	-10	-29	-11
300	256	6.14	Diclofenac 13C6	-173	-10	-15	-11
238.1	193	2.9	Dicrotophos.1	61	10	13	12
238.1	112.1	2.9	Dicrotophos.2	61	10	17	6
268.1	226.1	4.79	Diethofencarb.1	61	10	13	14
268.1	124	4.79	Diethofencarb.2	61	10	43	8
408.2	253.1	6.87	Difenoconazole Isomer 1.1*	46	10	31	6
406.1	251.1	6.87	Difenoconazole Isomer 1.2*	46	10	41	2
408.202	253.1	6.94	Difenoconazole Isomer 2.1*	46	10	31	6
406.101	251.1	6.94	Difenoconazole Isomer 2.2*	46	10	41	2
311	158.2	5.9	Diflubenzuron.1	61	10	19	10
311	141.1	5.9	Diflubenzuron.2	61	10	43	8
230	199	3.16	Dimethoate.1	46	10	13	12
230	125	3.16	Dimethoate.2	46	10	29	8
388.1	301	4.93	Dimethomorph Isomer 1.1*	75	10	29	0
388.1	165.1	4.93	Dimethomorph Isomer 1.2*	75	10	45	10
388.101	301	5.11	Dimethomorph Isomer 2.1*	75	10	29	0
388.101	165.1	5.11	Dimethomorph Isomer 2.2*	75	10	45	10
327.1	116	5.66	Dimoxystrobin.1	66	10	29	6
327.1	205	5.66	Dimoxystrobin.2	66	10	23	14
326.2	70.2	6.61	Diniconazole.1	72	10	50	3
326.2	159	6.61	Diniconazole.2	72	10	43	10

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
203.1	129.2	1.25	Dinotefuran.1	51	10	17	8
203.1	157.2	1.25	Dinotefuran.2	51	10	11	10
224.1	167	3.17	Dioxacarb.1	51	10	11	10
224.1	123	3.17	Dioxacarb.2	51	10	21	18
233	72	4.65	Diuron	169	10	25	13
233	133	4.65	Diuron 1	169	10	53	13
233.1	72	4.31	Diuron.1	71	10	37	14
235.1	72.1	4.31	Diuron.2	66	10	33	4
240	78	4.65	Diuron-d6	156	10	24	13
240	135	4.65	Diuron-d6	156	10	57	13
240	161	4.65	Diuron-d6	156	10	39	13
916.6	331.4	10.4	Doramectin.1	61	10	33	8
916.6	593.5	10.4	Doramectin.2	66	10	19	20
886.5	158.1	6.5	Emamectin-benzoate b1a.1	106	10	49	10
886.5	82.1	6.5	Emamectin-benzoate b1a.2	106	10	107	6
872.6	158.2	6	Emamectin-benzoate b1b.1	101	10	51	10
872.6	302.3	6	Emamectin-benzoate b1b.2	101	10	43	26
360.3	316.3	2.53	Enrofloxacin	120	10	25	13
360.3	342.3	2.53	Enrofloxacin 1	120	10	31	13
360.3	245.1	2.53	Enrofloxacin 2	120	10	38	13
330	121.1	5.42	Epoxiconazole.1	41	10	49	10
330	101.1	5.4	Epoxiconazole.2	41	10	69	2
914.6	186.2	9.97	Eprinomectin.1	66	10	25	12
914.6	154.2	9.97	Eprinomectin.2	66	10	49	10
734.5	576	4.01	Erythromycin	80	10	26	13
734.5	558	4.01	Erythromycin 1	80	10	25	13
736	578	4.01	Erythromycin 13C2	130	10	26	13
736	560	4.01	Erythromycin 13C2 1	130	10	26	13
736	160	4.01	Erythromycin 13C2 2	160	10	36	13
734.5	83	4.01	Erythromycin 2	80	10	95	13
734.5	158.2	4.01	Erythromycin 3	80	10	40	13
328.1	159	5.4	Etaconazole Isomer 1.1*	91	10	31	12
328.1	205	5.4	Etaconazole Isomer 1.2*	91	10	23	6
328.101	159	5.4	Etaconazole Isomer 2.1*	91	10	31	12
328.101	205	5.4	Etaconazole Isomer 2.2*	91	10	23	6
226.1	107.2	4.3	Ethiofencarb.1	56	10	21	6
226.1	164	4.3	Ethiofencarb.2	56	10	21	6
397.3	350.9	4.98	Ethiprole.1	96	10	27	10
397.3	255.2	4.98	Ethiprole.2	96	10	47	16
210.2	140.1	2.78	Ethirimol.1	96	10	31	8
210.2	98.1	2.78	Ethirimol.2	96	10	39	12
287.1	259.1	4.79	Ethofumesate.1	76	10	15	6
287.1	121.1	4.79	Ethofumesate.2	76	10	23	6
360.1	141	9	Etoxazole.1	31	10	59	8

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
360.1	57.2	9	Etoxazole.2	31	10	51	10
392	331	6.33	Famoxadone.1	46	10	13	10
392	238	6.33	Famoxadone.2	46	10	23	16
312.1	92	4.89	Fenamidone.1	36	10	35	6
312.1	236.1	4.89	Fenamidone.2	36	10	21	14
331	268	5.37	Fenarimol.1	81	10	35	26
331	81	5.37	Fenarimol.2	81	10	55	14
307.1	161.1	9.5	Fenazaquin.1	76	10	27	10
307.1	147	9.5	Fenazaquin.2	76	10	25	8
337	124.9	5.65	Fenbuconazole.1	61	10	55	14
337	70	5.65	Fenbuconazole.2	61	10	39	6
302	97	5.37	Fenhexamid.1	95	10	33	6
302	55	5.37	Fenhexamid.2	95	10	61	10
208.2	95.3	4.7	Fenobucarb.1	61	10	19	6
208.2	152.1	4.7	Fenobucarb.2	61	10	13	8
302.1	116.1	5.67	Fenoxycarb.1	61	10	17	6
302.1	88	5.67	Fenoxycarb.2	61	10	29	6
304	147	4.03	Fenpropimorph.1	141	10	39	12
304	117	4.03	Fenpropimorph.2	141	10	73	2
422	366.1	9.4	Fenpyroximate.1	88	10	23	10
422	135.1	9.4	Fenpyroximate.2	88	10	53	8
165.1	72.1	2.97	Fenuron.1	55	10	45	4
165.1	46	2.97	Fenuron.2	55	10	29	8
437.1	368	5.94	Fipronil.1	96	10	23	9
437.1	290	5.94	Fipronil.2	96	10	37	7
230.1	203.1	1.9	Flonicamid.1	71	10	23	12
230.1	174	1.9	Flonicamid.2	71	10	25	10
356	185	3	Florfenicol	-120	-10	-30	-11
356	336	3	Florfenicol 1	-120	-10	-13	-11
462.7	415.7	0	Fluazinam.1	-70	-10	-26	-11
462.7	397.8	0	Fluazinam.2	-70	-10	-24	-11
683.1	408	6.04	Flubendiamide.1	85	10	9	12
683.1	274.1	6.04	Flubendiamide.2	85	10	41	6
307.3	238.2	3.35	Fluconazole	70	10	24	13
307.3	220.3	3.35	Fluconazole 2	70	10	28	13
311	242.3	3.35	Fluconazole D4	60	10	25	13
266	227.1	5.08	Fludioxinil.1	41	10	11	12
266	229	5.08	Fludioxinil.2	41	10	17	14
364.1	152.1	5.27	Flufenacet.1	36	10	27	8
364.1	194.2	5.27	Flufenacet.2	36	10	17	12
489	158	9.54	Flufenoxuron.1	96	10	27	10
489	141.1	9.54	Flufenoxuron.2	96	10	63	8
233.1	72.1	4.31	Fluometuron.1	76	10	35	12
233.1	46	4.31	Fluometuron.2	76	10	37	8

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
459.2	427.2	5.28	Fluoxastrobin.1	81	10	23	12
459.2	188	5.28	Fluoxastrobin.2	81	10	47	10
376	307	5.27	Fluquinconazole.1	86	10	27	16
376	349	5.27	Fluquinconazole.2	86	10	29	20
316.1	165.1	5.66	Flusilazole.1	86	10	37	10
316.1	247.1	5.66	Flusilazole.2	86	10	21	18
324.1	242.1	5.08	Flutolanil.1	75	10	35	14
324.1	262.1	5.08	Flutolanil.2	75	10	31	16
302.1	70.1	4.5	Flutriafol.1	16	10	59	2
302.1	123	4.5	Flutriafol.2	16	10	37	2
248	129.1	4.6	Forchlorfenuron.1	71	10	25	8
248	93.1	4.6	Forchlorfenuron.2	71	10	49	6
222.1	165	0.4	Formetanate HCl.1	66	10	23	10
222.1	120	0.4	Formetanate HCl.2	66	10	37	8
185	157	1.54	Fuberidazole.1	86	10	37	8
185	65	1.54	Fuberidazole.2	86	10	57	12
302.1	242.1	4.71	Furalaxyl.1	51	10	21	16
302.1	95	4.71	Furalaxyl.2	51	10	39	8
383.1	195.1	7.5	Furathiocarb.1	86	10	25	12
383.1	252.1	7.5	Furathiocarb.2	86	10	17	6
172.3	137.2	0.6	Gabapentin	60	10	21	13
172.3	154.2	0.6	Gabapentin 1	60	10	16	13
249	121	7.3	Gemfibrozil	-100	-10	-30	-11
249	106	7.3	Gemfibrozil	-100	-10	-60	-11
255	121	7.3	Gemfibrozil d6	-100	-10	-20	-11
331.2	105	4.89	Halofenozide.1	30	10	23	6
331.2	275.1	4.89	Halofenozide.2	30	10	11	8
314.1	70	6.22	Hexaconazole.1	81	10	55	6
314.1	159	6.22	Hexaconazole.2	81	10	33	10
461.1	158.2	7.85	Hexaflumuron.1	85	10	23	10
461.1	141.1	7.85	Hexaflumuron.2	85	10	57	8
353.1	168	8.6	Hexythiazox.1	41	10	37	12
353.1	228	8.6	Hexythiazox.2	41	10	19	14
495.2	323.2	5.75	Hydramethylnon.1	136	10	41	10
495.2	151.1	5.75	Hydramethylnon.2	136	10	77	2
205	161	12.6	Ibuprofen	-132	-10	-10	-11
205	159	12.6	Ibuprofen	-132	-10	-10	-11
208	163	12.6	Iburpofen 13C3	-81	-10	-11	-11
297	159	3.74	Imazalil.1	81	10	29	12
297	201	3.74	Imazalil.2	81	10	25	12
256	209	3.1	Imidacloprid	60	10	21	13
256	175	3.1	Imidacloprid 1	60	10	27	13
256	209.1	3.07	Imidacloprid.1	61	10	21	14
256	175.1	3.07	Imidacloprid.2	61	10	25	10

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
260	213	3.1	Imidacloprid-d4	60	10	26	13
260	179	3.1	Imidacloprid-d4 1	60	10	29	13
528	203	7.23	Indoxacarb.1	55	10	47	12
528	218	7.23	Indoxacarb.2	55	10	35	16
334.2	70	6.97	Ipconazole Isomer 1.1*	81	10	37	12
334.2	125	6.97	Ipconazole Isomer 1.2*	101	10	47	12
334.201	70	7.31	Ipconazole Isomer 2.1*	81	10	37	12
334.201	125	7.31	Ipconazole Isomer 2.2*	101	10	47	12
321.2	119	5.17	Iprovalicarb Isomer 1.1*	61	10	47	8
321.2	203.1	5.17	Iprovalicarb Isomer 1.2*	61	10	13	14
321.201	119	5.16	Iprovalicarb Isomer 2.1*	61	10	47	8
321.201	203.1	5.16	Iprovalicarb Isomer 2.2*	61	10	13	14
307	231.1	4.51	Isocarbophos.1	32	10	19	5
307	121.1	4.51	Isocarbophos.2	32	10	42	7
194.1	95	4.41	Isoprocarb.1	56	10	21	6
194.1	137	4.41	Isoprocarb.2	56	10	13	8
207	72	4.54	Isoproturon	230	10	25	13
207	165	4.54	Isoproturon	230	10	20	13
207.2	72.1	4.51	Isoproturon.1	71	10	29	12
207.2	46.1	4.51	Isoproturon.2	71	10	35	8
210	75	4.54	Isoproturon-D3	199	10	25	13
210	168	4.54	Isoproturon-D3	199	10	21	13
892.6	569.5	10.6	Ivermectin.1	56	10	19	16
892.6	307.3	10.6	Ivermectin.2	56	10	31	8
531.3	81	4.08	Ketoconazole	120	10	144	13
531.3	489.3	4.08	Ketoconazole 1	120	10	50	13
535.3	493	4.08	Ketoconazole D4	100	10	45	13
535.3	81	4.08	Ketoconazole D4 1	100	10	120	13
314.2	116.1	5.66	Kresoxim-methyl.1	63	10	18	6
314.2	131.2	5.66	Kresoxim-methyl.2	63	10	29	8
205.2	89	0.42	Levamisole	100	10	85	13
205.2	178	0.42	Levamisole 1	100	10	30	13
249.1	182.1	4.23	Linuron.1	66	10	21	12
249.1	160	4.23	Linuron.2	66	10	25	34
511.1	158.1	9.2	Lufenuron.1	96	10	27	10
511.1	141.2	9.2	Lufenuron.2	96	10	61	8
412.1	328.1	4.99	Mandipropamid.1	85	10	19	8
412.1	356.1	4.99	Mandipropamid.2	85	10	15	10
363.2	72.1	1.11	Marbofloxacin	90	10	26	13
363.2	319.8	1.11	Marbofloxacin 1	90	10	22	13
363.2	345.3	1.11	Marbofloxacin 2	90	10	26	13
199	141	4.91	MCPA	-147	-10	-21	-11
199	105	4.91	MCPA	-147	-10	-40	-11

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
202	144	4.91	MCPA D3	-100	-10	-30	-11
202	108	4.91	MCPA D3 1	-100	-10	-45	-11
213	141	5.27	Mecoprop	-100	-10	-30	-11
213	71	5.27	Mecoprop 1	-100	-10	-15	-11
299	148.1	5.08	Mefenacet.1	36	10	21	8
299	120.1	5.08	Mefenacet.2	36	10	35	6
224	106	5.08	Mepanipyrim.1	86	10	35	6
224	77	5.08	Mepanipyrim.2	86	10	55	6
270.1	119.1	5.08	Mepronil.1	81	10	31	6
270.1	228	5.08	Mepronil.2	81	10	21	16
340.2	228.2	3.93	Mesotrione.1	85	10	22	5
340.2	104.1	3.93	Mesotrione.2	85	10	41	6
507.1	178.1	9	Metaflumizone.1	101	10	33	10
507.1	287.1	9	Metaflumizone.2	101	10	33	6
280.1	220.2	3.82	Metalaxyl.1	61	10	19	14
280.1	192.2	3.82	Metalaxyl.2	61	10	25	12
320.1	70	6.29	Metconazole.1	101	10	43	4
320.1	125	6.3	Metconazole.2	101	10	53	4
222.1	165.2	4.41	Methabenzthiazuron.1	46	10	21	10
222.1	150.3	4.41	Methabenzthiazuron.2	46	10	45	8
142	94	0.6	Methamidophos.1	51	10	19	6
142	125	0.6	Methamidophos.2	51	10	19	6
226	169	4.96	Methiocarb	30	10	12	13
226	121	4.96	Methiocarb 1	30	10	25	13
229	169	4.96	Methiocarb d3	110	10	71	13
229	121	4.96	Methiocarb d3 1	110	10	76	13
226.1	169.1	4.89	Methiocarb.1	56	10	13	10
226.1	121.1	4.89	Methiocarb.2	56	10	27	6
163.1	106	2	Methomyl.1	41	10	13	6
163.1	88.1	2	Methomyl.2	41	10	13	4
272.2	198	4.03	Methoprotryne.1	41	10	31	12
272.2	240.2	4.03	Methoprotryne.2	41	10	27	16
369.1	313.2	5.08	Methoxyfenozide.1	56	10	11	4
369.1	149.1	5.08	Methoxyfenozide.2	56	10	21	8
259	170.2	4.41	Metobromuron.1	60	10	25	10
259	148.2	4.41	Metobromuron.2	60	10	21	8
284	252	5.43	Metolachlor	200	10	22	13
284	176	5.43	Metolachlor	200	10	35	13
290	258	5.43	Metolachlor d6	196	10	20	13
268	91	0	Metopropol	261	10	68	13
268	103	0	Metopropol	261	10	57	13
275	122	0	Metopropol d7 1	274	10	26	13
215.1	187.1	3.93	Metribuzin.1	41	10	25	12
215.1	84.1	3.93	Metribuzin.2	41	10	31	6

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
225.101	127.1	3.21	Mevinphos Isomer 1.1*	56	10	21	8
225.101	193.2	3.21	Mevinphos Isomer 1.2*	56	10	11	12
225.102	127.1	3.55	Mevinphos Isomer 2.1*	56	10	21	8
225.102	193.2	3.55	Mevinphos Isomer 2.2*	56	10	11	12
223.2	166.1	1.15	Mexacarbate.1	56	10	21	10
223.2	151	1.15	Mexacarbate.2	56	10	31	10
417.2	159	4.83	Miconazole	160	10	40	13
417.2	161	4.83	Miconazole 1	160	10	43	13
417.2	89	4.83	Miconazole 2	160	10	116	13
693.4	479	10.12	Monensin	100	10	70	13
693.4	461	10.12	Monensin 1	100	10	70	13
693.4	675.6	10.12	Monensin 2	100	10	5	13
224.1	127.1	2.68	Monocrotophos.1	61	10	21	8
224.1	98	2.68	Monocrotophos.2	61	10	17	6
215.1	126.1	4.22	Monolinuron.1	61	10	23	8
215.1	99	4.22	Monolinuron.2	61	10	47	8
640.4	528.5	10.4	Moxidectin.1	61	10	13	18
640.4	498.5	10.4	Moxidectin.2	61	10	17	16
289	70	5.12	Myclobutanil.1	66	10	41	4
289	125	5.12	Myclobutanil.2	66	10	39	8
294.1	198.1	3.53	N-Acetyl-SMZ	-100	-10	-24	-11
294.1	133.8	3.53	N-Acetyl-SMZ	-100	-10	-31	-11
229	169	0	Naproxen	-100	-10	-47	-11
229	185	0	Naproxen	-100	-10	-10	-11
233	169	0	Naproxen 13C3	-42	-10	-46	-11
275	88	5.8	Neburon.1	26	10	23	6
275	114	5.8	Neburon.2	26	10	21	6
271	225.2	0.89	Nitenpyram.1	66	10	17	14
271	126	0.89	Nitenpyram.2	66	10	35	8
325.2	264.9	0	Norfloxacin D5	80	10	10	13
325.2	233.2	0	Norfloxacin D5 1	80	10	40	13
325.2	307.1	0	Norfloxacin D5 2	80	10	30	13
493	158.1	8.12	Novaluron.1	66	10	29	10
493	141.1	8.12	Novaluron.2	66	10	65	8
315	252.1	4.89	Nuarimol.1	101	10	37	22
315	81	4.89	Nuarimol.2	101	10	49	6
362	261	1.64	Ofloxacin	120	10	39	13
362	318	1.64	Ofloxacin	120	10	27	13
214	182.8	0.87	Omethoate.1	56	10	17	12
214	124.9	0.87	Omethoate.2	56	10	31	8
345	220	8.13	Oxadiazon	90	10	28	13
345	303	8.13	Oxadiazon 1	90	10	21	13
279.1	219.1	3.82	Oxadixyl.1	66	10	15	14

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
279.1	132.1	3.82	Oxadixyl.2	66	10	43	8
237.1	72.1	1.73	Oxamyl.1	26	10	29	4
237.1	90.1	1.73	Oxamyl.2	26	10	11	6
262.3	244.1	3.8	Oxolinic acid	90	10	28	13
262.3	216.3	3.8	Oxolinic acid 1	100	10	39	13
267.2	249.3	3.8	Oxolinic acid D5	50	10	30	13
267.2	161	3.8	Oxolinic acid D5 1	50	10	47	13
461	444	2.39	Oxytetracyclin	120	10	80	13
461	426.3	2.39	Oxytetracyclin	80	10	25	13
461	201.1	2.39	Oxytetracyclin 1	80	10	51	13
461	127.2	2.39	Oxytetracyclin 2	80	10	104	13
294	70	4.99	Paclobutrazol.1	21	10	49	12
294	125	4.99	Paclobutrazol.2	21	10	41	12
284.1	70	5.85	Penconazole.1	81	10	37	2
284.1	159	5.85	Penconazole.2	81	10	35	16
213	169	4.73	PFBA	-96	-10	-13	-11
217	172	4.73	PFBA 13C4	-99	-10	-13	-11
299	80	5.58	PFBS	-260	-10	-66	-11
299	99	5.58	PFBS	-260	-10	-39	-11
363	319	7.94	PFHpA	-116	-10	-14	-11
363	169	7.94	PFHpA	-116	-10	-24	-11
313	269	6.68	PFHxA	-107	-10	-12	-11
313	119	6.68	PFHxA	-107	-10	-28	-11
315	270	6.68	PFHxA 13C2	-60	-10	-13	-11
399	80	7.64	PFHxS	-260	-10	-93	-11
399	99	7.64	PFHxS	-260	-10	-66	-11
463	419	10.04	PFNA	-122	-10	-19	-11
463	219	10.04	PFNA	-122	-10	-25	-11
463	169	10.04	PFNA	-122	-10	-27	-11
468	423	10.04	PFNA 13C5	-57	-10	-16	-11
413	369	9.22	PFOA	-122	-10	-16	-11
413	169	9.22	PFOA	-122	-10	-26	-11
417	372	9.22	PFOA 13C4	-119	-10	-15	-11
499	80	9.8	PFOS	-260	-10	-97	-11
499	99	9.8	PFOS	-260	-10	-83	-11
503	80	9.8	PFOS 13C4	-276	-10	-104	-11
189.3	56	3	Phenazone	120	10	45	13
189.3	77	3	Phenazone 1	120	10	51	13
301.2	168	4.73	Phenmedipham.1	76	10	12	10
301.2	107.9	4.7	Phenmedipham.2	76	10	44	6
368	145	5.66	Picoxystrobin.1	56	10	29	8
368	205	5.66	Picoxystrobin.2	56	10	13	14
356.2	177.2	7.85	Piperonyl butoxide.1	41	10	13	10
356.2	119.1	7.85	Piperonyl butoxide.2	41	10	47	6

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
239.2	72.1	2.98	Pirimicarb.1	61	10	33	4
239.2	182.1	2.98	Pirimicarb.2	61	10	21	12
376	308	5.6	Prochloraz.1	51	10	15	8
376	70	5.6	Prochloraz.2	51	10	43	4
208.1	151	4.89	Promecarb.1	56	10	13	10
208.1	109	4.89	Promecarb.2	56	10	21	6
226.1	142	3.55	Prometon.1	81	10	33	8
226.1	86	3.55	Prometon.2	81	10	39	6
242.2	158.1	4.22	Prometryne.1	41	10	33	10
242.2	200.1	4.22	Prometryne.2	41	10	25	12
189.2	102	0.4	Propamocarb.1	61	10	25	6
189.2	144	0.4	Propamocarb.2	61	10	19	8
368.2	231.1	9.1	Propargite.1	41	10	15	16
368.2	175.1	9.1	Propargite.2	41	10	23	10
180.1	138	4.41	Propham.1	46	10	11	8
180.1	120	4.41	Propham.2	46	10	23	6
342.1	159	6.1	Propiconazole Isomer 1.1*	81	10	31	8
342.1	69	6.1	Propiconazole Isomer 1.2*	81	10	39	6
342.101	159	6.1	Propiconazole Isomer 2.1*	81	10	31	8
342.101	69	6.1	Propiconazole Isomer 2.2*	81	10	39	6
210.1	111	4.05	Propoxur.1	51	10	19	6
210.1	168.1	4.05	Propoxur.2	51	10	11	10
344.1	188.9	6.34	Prothioconazole.1	46	10	31	12
344.1	125.1	6.34	Prothioconazole.2	46	10	33	13
218	105	0.48	Pymetrozine.1	71	10	27	6
218	78	0.48	Pymetrozine.2	71	10	61	4
218.1	125	4.12	Pyracarbolid.1	61	10	25	8
218.1	97	4.12	Pyracarbolid.2	61	10	37	8
388	194	6.33	Pyraclostrobin.1	51	10	17	14
388	163	6.33	Pyraclostrobin.2	51	10	31	10
365	147	9.7	Pyridaben.1	41	10	33	8
365	309	9.7	Pyridaben.2	41	10	19	8
200	107	3.93	Pyrimethanil.1	86	10	33	6
200	82	3.93	Pyrimethanil.2	86	10	37	4
322	96	8.12	Pyriproxyfen.1	46	10	21	6
322	185	8.12	Pyriproxyfen.2	46	10	31	12
222	204	3.5	Quinmerac	50	10	23	13
222	140	3.5	Quinmerac 1	50	10	50	13
309.3	273.3	7.9	Quinoxyfen	100	10	38	13
309.3	197	7.9	Quinoxyfen 1	100	10	44	13
313	276.2	7.9	Quinoxyfen D4	80	10	35	13
313	163.2	7.9	Quinoxyfen D4 1	80	10	60	13
308.1	197.1	8.06	Quinoxyfen.1	91	10	45	12
308.1	162.1	8.06	Quinoxyfen.2	91	10	63	10

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
395.1	213.1	5.57	Rotenone.1	101	10	31	14
395.1	192.1	5.57	Rotenone.2	101	10	33	12
838	158.4	4.35	Roxithromycin 1	70	10	41	13
838	679.33	4.35	Roxithromycin 2	70	10	30	13
838	116.3	4.35	Roxitrhomycin	70	10	80	13
386.1	368.3	2.72	Sarafloxacin	120	10	33	13
386.1	299.1	2.72	Sarafloxacin 1	120	10	37	13
386.1	342.1	2.72	Sarafloxacin 2	120	10	28	13
226.2	170.1	3.55	Secbumeton.1	86	10	25	10
226.2	100	3.55	Secbumeton.2	86	10	37	6
233.3	137.2	4.84	Siduron.1	81	10	23	8
233.3	94	4.84	Siduron.2	81	10	31	6
202	104	4.08	Simazine	253	10	34	13
202	132	4.08	Simazine 1	253	10	26	13
205	70	4.08	Simazine 13C3	218	10	45	13
205	106	4.08	Simazine 13C3 1	218	10	35	13
214	124	3.46	Simetryn.1	36	10	29	10
214	144	3.46	Simetryn.2	36	10	29	8
748.5	142.2	5.44	Spinetoram.1	146	10	43	8
748.5	98.1	5.44	Spinetoram.2	146	10	95	8
732.5	142.2	5.04	Spinosad (Spinosyn A).1	136	10	39	14
732.5	98.1	5.04	Spinosad (Spinosyn A).2	136	10	95	6
746.8	142.4	5.4	Spinosad (Spinosyn D).1	112	11	41	11
746.8	98.3	5.4	Spinosad (Spinosyn D).2	112	11	93	7
411.3	71.3	9.4	Spirodiclofen.1	101	10	31	14
411.3	313.3	9.4	Spirodiclofen.2	101	10	17	6
371.2	273.2	8.95	Spiromesifen.1	76	10	11	8
371.2	255.2	8.95	Spiromesifen.2	76	10	31	6
374.2	330.2	5.3	Spirotetramat.1	136	10	23	8
374.2	302.2	5.3	Spirotetramat.2	136	10	27	20
298.2	144.2	4.13	Spiroxamine Isomer 1.1*	71	10	29	8
298.2	100.1	4.13	Spiroxamine Isomer 1.2*	71	10	43	6
298.201	144.2	4.13	Spiroxamine Isomer 2.1*	71	10	29	8
298.201	100.1	4.13	Spiroxamine Isomer 2.2*	71	10	43	6
582.3	236.3	0	Streptomycin	30	10	40	13
582.3	246.2	0	Streptomycin 1	30	10	48	13
582.3	540.4	0	Streptomycin 2	30	10	38	13
395	359	5.03	Sucralose	-145	-10	-17	-11
397	361	5.03	Sucralose 1	-145	-10	-17	-11
395	35	5.03	Sucralose 2	-145	-10	-16	-11
401	365	5.03	Sucralose d6	-160	-10	-16	-11
251	156	0	Sulfadiazine	60	10	19	13
251	99	0	Sulfadiazine 1	60	10	27	13
251	108	0	Sulfadiazine 2	60	10	34	13

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
311.3	156.2	3.67	Sulfadimethoxine	80	10	25	13
311.3	92	3.67	Sulfadimethoxine 1	80	10	45	13
311.3	108	3.67	Sulfadimethoxine 2	80	10	40	13
311.3	245	3.67	Sulfadimethoxine 3	80	10	25	13
279	92	2.57	Sulfamethazine	232	10	41	13
279	124	2.57	Sulfamethazine 1	232	10	32	13
285	70	2.57	Sulfamethazine 13C6	165	10	70	13
254	156	2.97	Sulfamethoxazole	150	10	22	13
254	92	2.97	Sulfamethoxazole	150	10	38	13
260	98	2.97	Sulfamethoxazole 13C6	70	10	36	13
256	92	1.34	Sulfathiazole	60	10	40	13
256	108.2	1.34	Sulfathiazole 1	60	10	40	13
256	156	1.34	Sulfathiazole 2	60	10	24	13
387	307.1	4.22	Sulfentrazone.1	96	10	29	20
387	146	4.22	Sulfentrazone.2	96	10	59	8
308.2	70	5.94	Tebuconazole.1	86	10	51	10
308.2	125	5.94	Tebuconazole.2	86	10	55	8
353.2	133	5.69	Tebufenozide.1	51	10	23	8
353.2	297.2	5.69	Tebufenozide.2	51	10	11	8
334	145	7.85	Tebufenpyrad.1	116	10	37	8
334	117	7.85	Tebufenpyrad.2	116	10	47	8
229.1	172.4	4.12	Tebuthiuron.1	66	10	25	10
229.1	116.1	4.12	Tebuthiuron.2	66	10	37	6
381.1	141.2	8.51	Teflubenzuron.1	106	10	47	8
381.1	158.2	8.51	Teflubenzuron.2	106	10	23	10
467	419.1	8.7	Temephos.1	96	10	27	12
467	405	8.7	Temephos.2	96	10	21	12
226.1	170.1	3.55	Terbumeton.1	41	10	23	10
226.1	100	3.55	Terbumeton.2	41	10	41	6
242	186	4.3	Terbutryn	255	10	25	13
242	91	4.3	Terbutryn	255	10	36	13
247	191	4.3	Terbutryn d5	228	10	27	13
247	91	4.3	Terbutryn d5 1	228	10	36	13
242.1	186.1	4.22	Terbutryn.1	36	10	25	12
242.1	68.1	4.22	Terbutryn.2	36	10	61	4
230	174	4.96	Terbutylazine	219	10	26	13
230	132	4.96	Terbutylazine	219	10	35	13
372.1	159	5.46	Tetraconazole.1	86	10	35	8
372.1	70	5.46	Tetraconazole.2	86	10	47	12
202.1	175.1	1.25	Thiabendazole.1	36	10	35	10
202.1	131.2	1.25	Thiabendazole.2	36	10	45	8
253	126	3.65	Thiacloprid.1	76	10	29	8
253	99	3.65	Thiacloprid.2	76	10	59	6
257	126	3.7	Thiacloprid-d4	100	10	28	13

Q1 (Da)	Q3 (Da)	Time (min)	ID	DP (V)	EP (V)	CE (V)	CXP (V)
257	73	3.7	Thiacloprid-d4 1	100	10	83	13
257	90	3.7	Thiacloprid-d4 2	100	10	54	13
292	211	2.5	Thiamethoxam.1	56	10	17	14
292	181	2.5	Thiamethoxam.2	56	10	31	12
295	214	2.5	Thiamethoxam-d3	70	10	19	13
295	132	2.5	Thiamethoxam-d3 1	70	10	30	13
221.1	102.1	4.12	Thidiazuron.1	36	10	23	6
221.1	127.9	4.12	Thidiazuron.2	36	10	23	8
258	125	6.33	Thiobencarb.1	40	10	23	8
258	89	6.33	Thiobencarb.2	40	10	65	6
219.2	57.2	4.31	Thiofanox.1	28	10	16	2
219.2	61.1	4.31	Thiofanox.2	28	10	13	2
343	151.1	4.13	Thiophanate-methyl.1	61	10	31	10
343	311	4.12	Thiophanate-methyl.2	61	10	17	8
424	424	6.46	Toltrazuril	-100	-10	-5	-11
427.2	427.2	6.46	Toltrazuril D3	-100	-10	-10	-11
294	197.1	4.12	Triadimefon.1	41	10	21	12
294	225	5.08	Triadimefon.2	41	10	19	14
296.1	70	5.12	Triadimenol.1	11	10	33	12
296.1	227.1	5.18	Triadimenol.2	11	10	17	16
256.9	109.1	2.99	Trichlorfon.1	66	10	25	6
256.9	127	2.99	Trichlorfon.2	66	10	23	8
190	163	3.64	Tricyclazole.1	76	10	33	10
190	136	3.64	Tricyclazole.2	76	10	39	8
409	186	7.04	Trifloxystrobin.1	61	10	21	12
409	206	7.04	Trifloxystrobin.2	61	10	19	14
346.1	278.1	6.13	Triflumizole.1	16	10	17	6
346.1	73	6.13	Triflumizole.2	16	10	27	4
359.1	156.2	6.61	Triflumuron.1	71	10	23	10
359.1	139	6.61	Triflumuron.2	71	10	45	8
291	123	0.9	Trimethoprim	293	10	34	13
291	230	0.9	Trimethoprim 1	293	10	33	13
294	126	0.9	Trimethoprim 13C3	221	10	33	13
294	233	0.9	Trimethoprim 13C3 1	221	10	32	13
318.1	70	5.32	Triticonazole.1	86	10	35	6
318.1	125	5.33	Triticonazole.2	86	10	49	8
288	146	3.26	Vamidothion.1	61	10	17	8
288	118	3.26	Vamidothion.2	61	10	37	8
336.1	187	6.14	Zoxamide.1	61	10	29	12
336.1	159	6.14	Zoxamide.2	61	10	55	10

Table A8: MS parameters of the GC multi-compound method

Compound	RT	Mass 1	Mass 2	Internal Standard
2,3,5,6-Tetrachloroaniline	13.99	230.99	232.97	Trifluralin-D14
2,6-Dichlorobenzonitrile (Dichlobenil)	7.99	171.05	172.98	Trifluralin-D14
2-Phenylphenol	11.6	170.04	169.10	Trifluralin-D14
3,4-Dichloroaniline	9.74	161.05	163.01	Trifluralin-D14
Acequinocyl	35.79	342.17	188.05	Iprodione-D5
Acetochlor	19.64	146.12	174.00	Propyzamide-D3
Acrinathrin	32.57	181.13	208.01	Iprodione-D5
Alachlor	20.01	188.01	160.12	Fenitrothion-D6
Aldrin	21.12	262.98	264.95	Fenitrothion-D6
Allidochlor	6.81	137.93	131.85	Trifluralin-D14
alpha-BHC	15.63	180.97	182.93	Trifluralin-D14
Anthraqinone	21.11	207.94	180.08	Fenitrothion-D6
Atrazine	16.79	200.04	202.09	Propyzamide-D3
Azinphos ethyl	32.38	132.00	159.64	Iprodione-D5
Azinphos methyl	31.09	132.00	159.64	Iprodione-D5
Benfluralin	15.5	292.03	264.11	Trifluralin-D14
beta-BHC	16.77	180.97	182.93	Propyzamide-D3
Bifenthrin	30.12	181.05	166.32	Iprodione-D5
Bioallethrin	23.33	79.00	122.97	Pendimethalin-D5
Biphenyl	8.69	154.00	153.25	Trifluralin-D14
Bromfenvinfos-methyl	23.14	294.95	296.91	Pendimethalin-D5
Bromfenvinphos	24.72	266.92	269.92	Pendimethalin-D5
Bromophos ethyl	23.88	358.76	356.80	Pendimethalin-D5
Bromophos methyl	22.2	330.92	329.03	Parathion-D10
Bromopropylate	29.86	340.92	338.99	Iprodione-D5
Bupirimate	25.73	272.92	208.13	Pendimethalin-D5
Captafol	28.66	79.01	275.83	Iprodione-D5
Captan	23.04	79.01	77.03	Pendimethalin-D5
Carbophenothion	27.58	341.67	343.70	Iprodione-D5
Carfentrazone ethyl	27.88	330.05	332.00	Iprodione-D5
Chlorbenside	23.45	125.03	126.99	Pendimethalin-D5
Chlorfenapyr	26.18	363.85	361.91	Pendimethalin-D5
Chlorfenson (Ovex)	24.53	174.84	176.84	Pendimethalin-D5
Chlorfenvinphos	23.21	266.99	268.96	Pendimethalin-D5
Chlorobenzilate	26.35	250.99	252.95	Pendimethalin-D5
Chloroneb	11.57	190.96	192.96	Trifluralin-D14
Chlorothalonil	18.17	266.01	264.07	Propyzamide-D3
Chlorpropham	14.7	212.77	214.80	Trifluralin-D14
Chlorpyrifos	21.63	313.74	315.78	Parathion-D10
Chlorpyrifos methyl	19.67	286.01	287.92	Fenitrothion-D6
Chlorthiophos (Isomer I)	27.01	268.95	270.93	Pendimethalin-D5
Chlorthiophos (Isomer II)	26.22	256.95	258.93	Pendimethalin-D5
Chlorthiophos (Isomer III)	26.52	268.95	270.93	Pendimethalin-D5

Compound	RT	Mass 1	Mass 2	Internal Standard
Chlozolinate	23.11	258.90	260.84	Pendimethalin-D5
cis-Chlordane	24.19	372.85	374.82	Pendimethalin-D5
cis-Nonachlor	26.68	408.82	406.88	Iprodione-D5
cis-Permethrin	33.4	183.06	165.10	Iprodione-D5
Clomazone (Command)	16.82	204.08	125.12	Propyzamide-D3
Coumaphos	33.74	361.88	363.91	Iprodione-D5
Cycloate	14.24	153.93	185.95	Trifluralin-D14
Cyfluthrin (Isomer 1)	34.61	206.11	199.13	Iprodione-D5
Cyfluthrin (Isomer 2)	34.8	206.11	199.13	Iprodione-D5
Cyfluthrin (Isomer 3)	34.94	206.11	199.13	Iprodione-D5
Cyfluthrin (Isomer 4)	35.02	206.11	199.13	Iprodione-D5
Cypermethrin (Isomer 1)	35.19	181.10	162.93	Iprodione-D5
Cypermethrin (Isomer 2)	35.39	181.10	162.93	Iprodione-D5
Cypermethrin (Isomer 3)	35.52	181.10	162.93	Iprodione-D5
Cyprodinil	22.54	224.20	225.13	Pendimethalin-D5
DCPA methyl ester (Chlorthal-dimethyl)	21.8	300.99	299.08	Parathion-D10
delta-BHC	17.98	180.97	182.93	Propyzamide-D3
Deltamethrin	38.35	250.84	254.78	Iprodione-D5
Diallate (cis)	15.57	233.99	235.96	Trifluralin-D14
Diallate (trans)	15.88	233.99	235.96	Trifluralin-D14
Diazinon	17.99	179.00	199.00	Propyzamide-D3
Dichlofluanid	21.03	223.88	225.92	Fenitrothion-D6
Dichloran	16.13	205.92	207.91	Trifluralin-D14
Dieldrin	25.02	262.96	263.91	Pendimethalin-D5
Dimethachlor	19.33	134.07	196.93	Propyzamide-D3
Diphenamid	22.3	167.11	165.24	Pendimethalin-D5
Diphenylamine	13.94	169.18	168.28	Trifluralin-D14
Disulfoton	17.99	96.99	87.89	Propyzamide-D3
Edifenphos	27.71	172.89	109.04	Iprodione-D5
Endosulfan ether	18.63	241.04	239.11	Propyzamide-D3
Endosulfan I	24.05	240.94	242.93	Pendimethalin-D5
Endosulfan II	26.17	240.93	242.96	Pendimethalin-D5
Endosulfan sulfate	27.74	271.89	273.90	Iprodione-D5
Endrin	25.8	316.83	314.85	Pendimethalin-D5
Endrin aldehyde	26.89	344.77	346.75	Iprodione-D5
Endrin ketone	29.38	316.86	318.81	Iprodione-D5
EPN	29.87	156.96	168.76	Iprodione-D5
Ethafluralin	15.01	276.05	315.95	Trifluralin-D14
Ethion	26.9	230.83	97.00	Iprodione-D5
Ethylan (Penthane)	26.11	223.13	236.11	Pendimethalin-D5
Etofenprox	35.71	162.99	135.08	Iprodione-D5
Etridiazole	10.29	210.88	212.85	Trifluralin-D14
Fenamiphos	24.69	303.05	288.05	Pendimethalin-D5
Fenarimol	32.05	139.00	141.00	Iprodione-D5
Fenchlorphos (Ronnel)	20.21	285.02	286.94	Fenitrothion-D6

Compound	RT	Mass 1	Mass 2	Internal Standard
Fenitrothion	20.79	259.94	276.78	Fenitrothion-D6
Fenpropathrin	30.29	181.12	264.98	Iprodione-D5
Fenson	21.96	267.80	269.76	Parathion-D10
Fenthion	21.52	277.94	169.06	Fenthion-D6
Fenvalerate (Isomer 1)	36.93	224.94	125.05	Iprodione-D5
Fenvalerate (Isomer 2)	37.33	224.94	125.05	Iprodione-D5
Fipronil	23.38	367.04	369.01	Pendimethalin-D5
Flochloralin	18.17	306.01	325.94	Propyzamide-D3
Fluazifop-butyl	26.23	282.05	254.18	Pendimethalin-D5
Flucythrinate (Isomer 1)	35.65	198.99	157.01	Iprodione-D5
Flucythrinate (Isomer 2)	36.03	198.99	157.01	Iprodione-D5
Fludioxonil	25.11	182.06	154.07	Pendimethalin-D5
Fluquinconazole	33.7	340.13	342.08	Iprodione-D5
Fluridone (Sonar)	36.36	328.23	329.18	Iprodione-D5
Flusilazole	25.57	233.11	206.15	Pendimethalin-D5
Flutolanil	24.86	173.03	280.95	Pendimethalin-D5
Flutriafol	24.4	123.01	164.06	Pendimethalin-D5
Folpet	23.29	259.85	261.88	Pendimethalin-D5
Fonofos	17.39	136.79	108.94	Propyzamide-D3
gamma-BHC (Lindane)	16.98	180.97	182.93	Propyzamide-D3
Heptachlor	19.81	271.86	273.85	Fenitrothion-D6
Heptachlor epoxide (isomer B)	22.71	352.82	354.78	Pendimethalin-D5
Hexachlorobenzene	15.9	284.13	285.96	Trifluralin-D14
Hexazinone (Velpar)	28.41	171.03	128.10	Iprodione-D5
Iodofenphos	24.7	376.92	378.90	Pendimethalin-D5
Iprodione	29.55	313.94	315.92	Iprodione-D5
Isazophos	18.45	256.73	258.77	Propyzamide-D3
Isodrin	22.24	193.05	195.03	Pendimethalin-D5
Isopropalin	22.63	280.03	238.09	Pendimethalin-D5
lambda-Cyhalothrin	32.1	181.15	196.97	Iprodione-D5
Lenacil	27.9	153.04	154.05	Iprodione-D5
Leptophos	31.17	976.99	375.05	Iprodione-D5
Linuron	20.86	186.99	188.95	Fenitrothion-D6
Malathion	21.3	172.78	126.83	Malathion-D10
Metalaxyl	20.27	205.98	160.08	Fenitrothion-D6
Metazachlor	22.74	208.90	210.92	Pendimethalin-D5
Methacrifos	11.45	207.71	179.86	Trifluralin-D14
Methoxychlor	30.12	227.00	228.13	Iprodione-D5
Methyl parathion	19.65	262.75	108.98	Fenitrothion-D6
Metolachlor	21.39	162.10	237.97	Pendimethalin-D5
Mevinphos (E isomer)	9.83	126.95	191.75	Trifluralin-D14
Mevinphos (Z isomer)	9.77	126.95	191.75	Trifluralin-D14
MGK-264 (Isomer 1)	22.19	163.94	210.07	Pendimethalin-D5
MGK-264 (Isomer 2)	22.62	163.94	210.07	Pendimethalin-D5
Mirex	31.31	271.88	273.84	Iprodione-D5

Compound	RT	Mass 1	Mass 2	Internal Standard
Myclobutanil	25.43	178.98	180.96	Pendimethalin-D5
N-(2,4-Dimethylphenyl)formamide	10.84	120.05	148.92	Trifluralin-D14
Nitralin	29.29	274.01	315.94	Iprodione-D5
Nitrofen	25.84	282.96	284.93	Pendimethalin-D5
Norflurazon	27.92	303.01	145.07	Iprodione-D5
o,p'-DDD	25.41	235.03	236.99	Pendimethalin-D5
o,p'-DDE	23.92	317.90	315.93	Pendimethalin-D5
o,p'-DDT	26.74	235.05	237.03	Pendimethalin-D5
o,p'-Methoxychlor	28.48	307.97	309.97	Iprodione-D5
Oxadiazon	25.4	174.94	176.93	Pendimethalin-D5
Oxyfluorfen	25.63	252.12	300.80	Pendimethalin-D5
p,p'-DDD	26.66	235.06	237.02	Pendimethalin-D5
p,p'-DDE	25.11	317.97	316.01	Pendimethalin-D5
p,p'-DDT	27.99	235.05	237.04	Pendimethalin-D5
p,p'-Methoxychlor olefin	27.77	308.04	238.21	Iprodione-D5
Paclobutrazol	23.92	235.92	237.95	Pendimethalin-D5
Parathion (ethyl parathion)	21.64	290.67	108.97	Parathion-D10
Pebulate	10.44	127.88	159.92	Trifluralin-D14
Penconazole	22.87	248.09	250.08	Pendimethalin-D5
Pendimethalin	22.86	251.93	208.15	Pendimethalin-D5
Pentachloroaniline	18.8	265.02	266.95	Propyzamide-D3
Pentachloroanisole	16.14	265.14	267.06	Trifluralin-D14
Pentachlorobenzene	11.77	250.02	251.92	Trifluralin-D14
Pentachlorobenzonitrile	17.25	275.02	276.96	Propyzamide-D3
Pentachloronitrobenzene (quintozene)	17.19	248.92	250.91	Propyzamide-D3
Pentachlorothioanisole	20.78	295.91	297.86	Fenitrothion-D6
Phenothrin (cis)	30.82	183.04	123.00	Iprodione-D5
Phenothrin (trans)	31.03	183.04	123.00	Iprodione-D5
Phorate	15.57	230.77	96.92	Trifluralin-D14
Phosalone	31.14	181.93	183.92	Iprodione-D5
Phosmet	29.69	160.03	133.07	Iprodione-D5
Piperonyl butoxide	28.96	176.03	149.06	Iprodione-D5
Pirimiphos ethyl	22.6	318.00	332.81	Pendimethalin-D5
Pirimiphos methyl	20.95	290.01	276.06	Fenitrothion-D6
p-p'-Dichlorobenzophenone	21.62	139.00	141.99	Parathion-D10
Pretilachlor	25.15	176.11	202.09	Pendimethalin-D5
Prochloraz	33.85	307.91	309.90	Iprodione-D5
Procymidone	23.49	282.91	284.90	Pendimethalin-D5
Prodiamine	21.03	320.99	333.10	Fenitrothion-D6
Profenofos	24.98	336.80	338.78	Pendimethalin-D5
Profluralin	17.65	318.07	330.01	Propyzamide-D3
Propachlor	13.78	120.04	175.90	Trifluralin-D14
Propanil	19.33	161.05	163.03	Propyzamide-D3
Propargite (Isomer 1)	28.72	135.02	173.00	Iprodione-D5
Propargite (Isomer 2)	28.77	135.02	173.00	Iprodione-D5

Compound	RT	Mass 1	Mass 2	Internal Standard
Propisochlor	20.19	162.08	222.96	Fenitrothion-D6
Propyzamide	17.5	173.04	174.99	Propyzamide-D3
Prothiofos	24.85	308.82	310.86	Pendimethalin-D5
Pyraclofos	32.66	359.94	361.94	Iprodione-D5
Pyrazophos	32.47	221.06	232.05	Iprodione-D5
Pyridaben	33.55	147.02	308.97	Iprodione-D5
Pyridafenthion	29.72	339.90	199.07	Iprodione-D5
Pyrimethanil	17.64	198.21	199.12	Propyzamide-D3
Pyriproxyfen	31.37	136.03	226.03	Iprodione-D5
Quinalphos	23.3	146.00	156.00	Pendimethalin-D5
Resmethrin (cis Isomer)	28.87	143.04	128.10	Iprodione-D5
Resmethrin (trans Isomer)	29.09	143.04	128.10	Iprodione-D5
Sulfotepp	15.5	321.77	293.81	Trifluralin-D14
Sulprofos	27.27	156.00	321.84	Iprodione-D5
tau-Fluvalinate (Isomer 1)	37.37	250.08	252.05	Iprodione-D5
tau-Fluvalinate (Isomer 2)	37.51	250.08	252.05	Iprodione-D5
Tebuconazole	28.47	249.99	251.96	Iprodione-D5
Tebufenpyrad	30.39	332.95	334.98	Iprodione-D5
Tefluthrin	18.52	177.06	196.93	Propyzamide-D3
Terbacil	18.23	161.00	162.97	Propyzamide-D3
Terbufos	17.33	230.80	232.82	Propyzamide-D3
Terbuthylazine	17.39	214.03	216.09	Propyzamide-D3
Tetrachloronitrobenzene (Tecnazene)	13.57	214.92	216.88	Trifluralin-D14
Tetrachlorvinfos	24.2	329.02	330.96	Pendimethalin-D5
Tetradifon	30.77	226.93	228.91	Iprodione-D5
Tetramethrin (Isomer 1)	29.82	164.00	123.04	Iprodione-D5
Tetramethrin (Isomer 2)	30.08	164.00	123.04	Iprodione-D5
THPI (Tetrahydrophthalimide)	10.85	150.89	122.93	Trifluralin-D14
Tolclofos-methyl	19.81	265.03	266.96	Fenitrothion-D6
Tolyfluanid	23.03	237.86	239.83	Pendimethalin-D5
trans-Chlordane	23.61	372.89	374.85	Pendimethalin-D5
Transfluthrin	20.05	163.02	334.67	Fenitrothion-D6
trans-Nonachlor	24.38	408.85	406.98	Pendimethalin-D5
trans-Permethrin	33.67	183.06	165.10	Iprodione-D5
Triadimefon	21.74	207.92	209.92	Parathion-D10
Triadimenol	23.29	128.01	112.03	Pendimethalin-D5
Triallate	18.36	267.99	269.94	Propyzamide-D3
Triazophos	27.38	161.01	256.79	Iprodione-D5
Tricyclazole (Beam)	24.79	188.94	161.07	Pendimethalin-D5
Triflumizole	23.73	206.04	218.07	Pendimethalin-D5
Trifluralin	15.41	264.06	305.96	Trifluralin-D14
Vinclozolin	19.69	212.03	214.02	Fenitrothion-D6

Table A9: Experimental LOQ for substances analysed by GC-ion trap-MS

Compound	Urine (ng/l)	Water (ng/l)	Soil (ng/kg)	Liquid manure (ng/l)	Solid manure (ng/kg)
Anthraqinone	200	4	80	200	4000
Chlorpyrifos	500	10	200	500	10000
cis-Chlordane	125	3	50	125	2500
Cypermethrin	2500	50	1000	2500	50000
Flusilazole	2500	50	1000	2500	50000
Hexachlorobenzene	50	1	20	50	1000
Metazachlor	5000	100	2000	5000	100000
Metolachlor	500	10	200	500	10000
o,p'-DDT	500	10	200	500	10000
p,p'-DDD	250	5	100	250	5000
p,p'-DDE	250	5	100	250	5000
p,p'-DDT	500	10	200	500	10000
Tebuconazole	5000	100	2000	5000	100000
Trifluralin	500	10	200	500	10000
All other substances(*)	2500	50	1000	2500	50000

(*) extrapolated from lower level of calibration curve

Table A10: Experimental LOQ for substances analysed by LC-MS/MS

Analyte	Urine (ng/l)	Water (ng/l)	Soil (ng/kg)	Liquid manure (ng/l)	Solid manure (ng/kg)
2,4,5-T	10	0.1	2	10	100
2,4-D	100	1	20	100	1000
Acesulfame K	10	0.1	2	10	100
Azoxystrobin	4	0.04	0.8	4	40
Benzotriazole	40	0.4	8	40	400
Boscalid	4	0.04	0.8	4	40
Carbendazim	0.5	0.005	0.1	0.5	5
Chlarithromycin	200	2	40	200	2000
Chloridazon	300	3	60	300	3000
Chlorotoluron	1	0.01	0.2	1	10
Chlothianidin	4	0.04	0.8	4	40
Climbazole	10	0.1	2	10	100
Cyproconazole	4	0.04	0.8	4	40
Diclofenac	100	1	20	100	1000
Dimoxystrobin	1	0.01	0.2	1	10
Diuron	0.9	0.01	0.18	0.9	9
Epoxiconazole	4	0.04	0.8	4	40
Fluconazole	4	0.04	0.8	4	40
Fluometuron	2	0.02	0.4	2	20
Furathiocarb	0.4	0.004	0.08	0.4	4
Imidacloprid	4	0.04	0.8	4	40
Isoproturon	1	0.01	0.2	1	10

Analyte	Urine (ng/l)	Water (ng/l)	Soil (ng/kg)	Liquid manure (ng/l)	Solid manure (ng/kg)
Metaflumizone	20	0.2	4	20	200
Metconazole	0.5	0.005	0.1	0.5	5
Methoxyfenozide	2	0.02	0.4	2	20
Methoxyfenozide	0.4	0.004	0.08	0.4	4
Metolachlor	25	0.25	5	25	250
Miconazole	30	0.3	6	30	300
Monensin	3	0.03	0.6	3	30
N-Acetyl-Sulfamethoxazole	4	0.04	0.8	4	40
Oxadiazon	6	0.06	1.2	6	60
Oxolinic acid	10	0.1	2	10	100
Oxytetracycline	130	1.3	26	130	1300
PFHpA	30	0.3	6	30	300
PFHxA	17	0.2	3	17	170
PFNA	100	1	20	100	1000
PFOA	50	0.5	10	50	500
Piperonyl butoxide	1.3	0.01	0.26	1.3	13
Prometon	1	0.01	0.2	1	10
Prometryn	0.1	0.001	0.02	0.1	1
Propiconazole Isomer 1	1.3	0.01	0.26	1.3	13
Secbumeton	0.7	0.01	0.14	0.7	7
Spiroxamine isomer 1	0.2	0.002	0.04	0.2	2
Spiroxamine isomer 2	0.2	0.002	0.04	0.2	2
Sulfamethazine	0.5	0.005	0.1	0.5	5
Sulfamethoxazole	7	0.07	1.4	7	70
Tebuconazole	4	0.04	0.8	4	40
Terbutryn	0.5	0.005	0.1	0.5	5
Tetraconazole	0.6	0.006	0.12	0.6	6
Thiabendazole	2	0.02	0.4	2	20
Tricyclazole	0.6	0.006	0.12	0.6	6
All other substances	4	0.04	0.8	4	40

(*) extrapolated from lower level of calibration curve

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